

CHEMISTRY OF COAL UTILIZATION

VOLUME I

PREPARED BY THE COMMITTEE
ON CHEMICAL UTILIZATION OF
COAL, DIVISION OF CHEMISTRY
AND CHEMICAL TECHNOLOGY,
NATIONAL RESEARCH COUNCIL.
. H. H. LOWRY, CHAIRMAN

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PREFACE

At its meeting in November 1937, the Division of Chemistry and Chemical Technology of the National Research Council, recognizing the importance of chemistry to coal technology, voted to organize a Committee on Chemical Utilization of Coal. Subsequently, the following Committee was appointed and given the responsibility of determining what it might accomplish.

Chairman:

H. H. Lowry, Director, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

Members:

Fred Denig, Vice-President, Koppers Company, Pittsburgh, Pa.

W. S. Landis,* Vice-President, American Cyanamid Company, New York, N. Y.

A. R. Powell, Chief Chemical Engineer, Koppers Company, Pittsburgh, Pa.

F. H. Reed, Chief Chemist, Illinois Geological Survey, Urbana, Ill.

R. P. Russell, Vice-President, Standard Oil Development Company, New York, N. Y.

H. H. Storch, Principal Physical Chemist, U. S. Bureau of Mines, Pittsburgh, Pa.

C. E. Williams, Director, Battelle Memorial Institute, Columbus, O.

Discussion among the Committee members and with other individuals active in scientific and technical aspects of coal utilization led to the decision that the greatest service would be the preparation of a comprehensive, but critical, review of the vast literature that has accumulated on the chemistry of coal utilization. No such review existed in any language. Several books and monographs on special topics were available, most of which, however, treated the work done only in a certain country or by a certain "school" with infrequent reference to other work.

Coal has world-wide distribution, and upon its use depend the industrial welfare and comfort of the greater part of the world's population. As a logical consequence, studies of coal and its utilization have been made throughout the world. Nevertheless, the nature of coal is incompletely understood, and most of coal technology re-

* Deceased.

mains as much an art as a science. A review of the studies already made should serve to put the available data in perspective from which further advances in coal technology should follow.

In all its uses coal undergoes a series of chemical reactions, and, since these are predominantly heterogeneous reactions, the physical as well as the chemical properties of coal are of great importance. Consequently, it seemed essential to include in the review, as relevant subjects, the origin and classification of coals, and the physical properties of coal, together with the chemical nature of coal, and the chemistry of coal carbonization, combustion, gasification, and hydrogenation.

The Committee, having decided on an objective, gave much consideration to its most effective realization. It was clearly recognized that the literature on the chemistry of coal utilization was too extensive for any one person to cover satisfactorily. Accordingly, an outline, presenting 38 separate topics, together with the names of persons qualified to prepare reviews of the topics, was circulated in September 1938 to the members of the Committee for suggestion, modification, and amplification. Full cooperation of each member of the Committee was received, an unusual manifestation of acceptance of the responsibility of committee membership that was deeply appreciated by the Chairman. The replies were collected and a new outline prepared listing all suggested collaborators. The new outline was discussed at a meeting of the Committee in April 1939, and a decision was reached, in the main, on the subjects to form individual chapters in the final review and on the persons to be invited to participate in the work.

An outline of the proposed review was next sent to each of the prospective authors of the individual chapters, and their collaboration was requested. In these negotiations it was pointed out that the review was to cover the literature through 1939 and to be in the hands of the Chairman by July 1, 1940. Suggestions were also solicited for making the review as complete as possible, and several additional chapters were added as a result. The response was extremely gratifying, all requests but one being accepted. However, with the outbreak of war in Europe in 1939 and the consequent increased demands on already busy people, delays in receipt of manuscript were encountered, and the final manuscript was not received until July 1943. Also, certain individuals were unable to fulfill their original commitments, and it became necessary to secure alternates or to add co-authors to complete the manuscripts.

From 1939 to 1942, the following individuals were appointed to the Committee on Chemical Utilization of Coal, in addition to the original membership:

- E. P. Barrett, Mellon Institute, Pittsburgh, Pa.
 C. C. Boley, Illinois Geological Survey, Urbana, Ill.
 R. E. Brewer, U. S. Bureau of Mines, Pittsburgh, Pa.
 Gilbert Cady, Illinois Geological Survey, Urbana, Ill.
 J. D. Davis, U. S. Bureau of Mines, Pittsburgh, Pa.
 A. C. Fieldner, U. S. Bureau of Mines, Washington, D. C.
 C. H. Fisher, U. S. Bureau of Agricultural Chemistry and Engineering,
 Philadelphia, Pa.
 A. W. Gauger, Pennsylvania State College, State College, Pa.
 W. L. Glowacki, Mellon Institute, Pittsburgh, Pa.
 H. A. Gollmar, Koppers Company, Pittsburgh, Pa.
 T. A. Hendricks, U. S. Geological Survey, Washington, D. C.
 W. H. Hill, Mellon Institute, Pittsburgh, Pa.
 L. L. Hirst, U. S. Bureau of Mines, Pittsburgh, Pa.
 H. C. Hottel, Massachusetts Institute of Technology, Cambridge,
 Mass.
 H. C. Howard, Coal Research Laboratory, Carnegie Institute of Tech-
 nology, Pittsburgh, Pa.
 M. W. Kiebler, Coal Research Laboratory, Carnegie Institute of Tech-
 nology, Pittsburgh, Pa.
 W. R. Kirner, Coal Research Laboratory, Carnegie Institute of Tech-
 nology, Pittsburgh, Pa. (National Defense Research Committee,
 Washington, D. C.*)
 M. A. Mayers, Coal Research Laboratory, Carnegie Institute of Tech-
 nology, Pittsburgh, Pa. (Elliott Company, Jeannette, Pa.)*
 L. C. McCabe, Illinois Geological Survey, Urbana, Ill. (U. S. Army,
 Washington, D. C.)*
 W. F. McCutcheon, Mellon Institute, Pittsburgh, Pa.
 J. J. Morgan, Columbia University, New York, N. Y.
 A. A. Orning, Coal Research Laboratory, Carnegie Institute of Tech-
 nology, Pittsburgh, Pa.
 E. O. Rhodes, Koppers Company, Pittsburgh, Pa.
 H. J. Rose, Mellon Institute, Pittsburgh, Pa. (Bituminous Coal Re-
 search, Inc., Pittsburgh, Pa.)*
 R. W. Ryan, Consolidated Edison Company, New York, N. Y.
 L. D. Schmidt, U. S. Bureau of Mines, Pittsburgh, Pa.
 W. A. Selvig, U. S. Bureau of Mines, Pittsburgh, Pa.
 Louis Shnidman, Rochester Gas and Electric Corporation, Rochester,
 N. Y.
 Gilbert Thiessen, Koppers Company, Pittsburgh, Pa.
 B. J. C. van der Hoeven, Koppers Company, Pittsburgh, Pa.
 J. F. Weiler, Coal Research Laboratory, Carnegie Institute of Tech-
 nology, Pittsburgh, Pa. (Mathieson Alkali Works, Inc., Buffalo,
 N. Y.)*
 P. J. Wilson, Jr., Mellon Institute, Pittsburgh, Pa.
 H. F. Yancey, U. S. Bureau of Mines, Seattle, Washington.

* Present address.

In addition to the above membership, M. R. Geer of the U. S. Bureau of Mines, Seattle, Washington, F. H. Gibson, U. S. Bureau of Mines, Pittsburgh, Pa., J. H. Wells, Mellon Institute, Pittsburgh, Pa., and John O'Brochta and Susan E. Woodridge of the Koppers Company, Pittsburgh, Pa., collaborated with the Committee as co-authors of Yancey, Selvig, Wilson, and Rhodes, respectively.

Dr. H. H. Storch was appointed Vice-Chairman of the Committee in December 1940. The Committee membership was decreased late in 1942 to H. H. Lowry, Chairman, H. H. Storch, Vice-Chairman, and A. R. Powell.

Late in 1939, on vote of the membership of the Committee, an Editorial Committee was formed: Fieldner, Lowry (Chairman), Rose, Storch, and Thiessen. This committee met early in 1940 to consider the authors' estimates of the length of their respective chapters, and several revisions in these estimates were suggested. It was decided to submit the manuscript of each chapter as received to two reviewers for criticisms and to return the manuscript to the author with the criticisms. The final responsibility of accepting or rejecting any proposed alteration on the basis of the reviewer's criticism was to be that of the author. This procedure, though most helpful, was discontinued in 1942 in order not to delay unduly the completion of the manuscript. The Editorial Committee decided also that, in literature citations, the author's name should be followed by his initials, that inclusive pages should be given, that the abbreviations should be those used by *Chemical Abstracts* as given in the "List of Periodicals" of November 20, 1936, and in the "Supplement to the List of Periodicals Abstracted" of December 20, 1942, and that references to the patent literature should include the inventor's name and initials, the patent number, and the year of issue. These procedures have been followed as far as possible and have eliminated, in a large measure, copying references from secondary sources where they are generally incomplete and frequently incorrect.

The reviewers of the individual chapters were selected by the Editorial Committee, and grateful acknowledgment of the Committee on Chemical Utilization of Coal is hereby made not only to those of its membership who participated in the review of the manuscripts, but also to the following:

F. M. Becker, U. S. Steel Corporation, Pittsburgh, Pa.
W. T. Brown, Jones & Laughlin Steel Corporation, Pittsburgh, Pa.
H. L. Brunjes, Fuel Engineering Company, New York, N. Y.
A. N. Cole, Carnegie-Illinois Steel Corporation, Gary, Ind.
Gustav Egloff, Universal Oil Products Company, Chicago, Ill.
Abner Eisner, U. S. Bureau of Mines, Pittsburgh, Pa.
P. H. Emmett, Johns Hopkins University, Baltimore, Md.
W. M. Fuchs, Pennsylvania State College, State College, Pa.

R. M. Hardgrove, Babcock & Wilcox Company, New York, N. Y.
H. F. Hebley, Pittsburgh Coal Company, Pittsburgh, Pa.
W. W. Hodge, West Virginia University, Morgantown, W. Va.
I. H. Jones, Koppers Company, Pittsburgh, Pa.
F. W. Jung, Koppers Company, Kearny, N. J.
C. D. King, U. S. Steel Corporation, Pittsburgh, Pa.
A. T. Larson, E. I. duPont de Nemours & Company, Wilmington, Del.
P. V. Martin, Carnegie-Illinois Steel Corporation, Gary, Ind.
D. R. Mitchell, Pennsylvania State College, State College, Pa.
Percy Nicholls,* U. S. Bureau of Mines, Pittsburgh, Pa.
J. H. H. Nicolls, Department of Mines & Resources, Ottawa, Canada.
J. D. Piper, Detroit Edison Company, Detroit, Mich.
H. C. Porter,* Philadelphia, Pa.
O. W. Rees, Illinois Geological Survey, Urbana, Ill.
W. C. Schroeder, U. S. Bureau of Mines, College Park, Md.
J. A. Shaw, Mellon Institute, Pittsburgh, Pa.
R. A. Sherman, Battelle Memorial Institute, Columbus, O.
G. C. Sprunk, U. S. Bureau of Mines, Pittsburgh, Pa.
Edgar Stansfield, Research Council of Alberta, Edmonton, Alberta, Canada.
G. B. Taylor, E. I. duPont de Nemours & Company, Wilmington, Del.
T. E. Warren, Department of Mines and Resources, Ottawa, Canada.
G. R. Yohe, Illinois Geological Survey, Urbana, Ill.

Throughout the period of organization of the Committee and preparation of this report, the interest and help of the Chairmen of the Division of Chemistry and Chemical Technology of the National Research Council, Dr. Herbert R. Moody and Dr. W. Mansfield Clark, and of other officers of the National Research Council have been much appreciated. Since the Division could not provide funds either for preparation of the manuscript and the illustrations for the printer or for the publication of the complete manuscript, negotiations were entered into with three commercial publishers, all of whom showed great interest in the work. A contract for publication of the *Chemistry of Coal Utilization* between the National Research Council and John Wiley & Sons was signed in 1942.

One of the objectives of the Committee has been to make available as widely as possible the knowledge that has been gained from the study of coal and of its utilization. Every effort therefore has been made to keep the price of the report as low as is consistent with maintaining good workmanship. No royalties are to be paid by the publisher either to the National Research Council or to any individual contributor, nor are reprints of the individual chapters to be made available to the authors. The publisher agreed to meet the cost, estimated before the completion of the manuscript, of retyping such parts as might prove necessary to provide the printer with clean copy

* Deceased.

and of redrawing the illustrations for the engraver. These actual costs exceeded the estimate by \$1,000 and this excess was covered by a contribution from the Koppers Company of Pittsburgh, Pennsylvania. This contribution has reduced the price of these volumes by an amount greater than the actual sum involved, and this generous action of the Koppers Company has directly helped the Committee to realize the objective stated in the first sentence of this paragraph.

In a work such as this, with so many collaborators, uniform treatment of the subjects is not to be expected. Each author, who was selected because he was directly engaged in or closely associated with work on the subject of his chapter, was asked not only to discuss its status as disclosed by the literature, but also to point out where additional information would be helpful in advancing knowledge of the subject. The original intention, as previously stated, was to include consideration of all published material through 1939. The manuscripts of many chapters, receipt of which was delayed, included references of papers published in 1942 to 1943. In other chapters, later references were added editorially to those cited in the original manuscript, and, where possible, statistical information was brought up to the latest available at the time of galley proof. Many authors requested permission, which was gratefully granted, to use unpublished data.

Reading of galley and page proof and checking illustrations were done by the Editor, who also prepared the book index, the name index, and the subject index. The book index is a list of all books and monographs referred to in the text, except bulletins, technical papers, and similar serial publications. It was felt that such a list would be of value to all organizations maintaining a library relating to coal and its utilization. The value of a name index has been questioned, but for the many who, like the Editor, associate names with specific information, it has been included. A subject index is always a compromise between completeness and expediency; that included herein was prepared by the Editor with the assistance of the individual authors in most cases.

Though each author is to be regarded as solely responsible for the conclusions drawn in his chapter, the Editor must acknowledge responsibility for many changes which were made primarily in an attempt at uniformity of style. Incomplete or incorrect references were emended by the Editor. Since each author saw only galley proof of his chapter and not the edited manuscript, an indeterminate share of the responsibility for correctness of statement and citation must be acknowledged by the Editor. Care was taken not to change any expression of personal opinion by an author even though the opinion was distinctly contrary to that held by the Editor.

Differences in opinion held on the same subjects by different authors

are evident in many of the chapters where the same experimental data are considered in relation to different topics; they indicate the need for additional facts so that only a unique interpretation is possible. It is this frequent consideration of experimental work in a particular field by more than one author that renders less important the fact that not all of the authors were equally thorough in their reviews of the literature on the subjects of their chapters. Cross references are given in limited number in the text; further cross referencing is available through the subject index.

The Editor's opinion is that a work of this kind might, if the demand appeared, be reprinted, but that a new edition should be unnecessary. *Chemistry of Coal Utilization* should be kept up to date with supplementary monographs on the subjects forming individual chapters or groups of chapters in the present volumes. Errors of omission and commission should be corrected in the supplementary volumes, and it would be greatly appreciated by the Editor if the readers of these volumes would call his attention to errors.

To all those who have contributed so generously to this cooperative work the Committee on Chemical Utilization of Coal acknowledges its gratitude.

H. H. LOWRY

*Editor and Chairman of Committee
on the Chemical Utilization of Coal,
Division of Chemistry and Chemical
Technology, National Research
Council*

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CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH, PENNSYLVANIA
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CHAPTER 1

THE ORIGIN OF COAL *

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The origin of coal might be explained adequately for some purposes by the simple statement that coal is formed from accumulations of plant materials that were preserved from complete decay and later altered by various chemical and physical agencies. For the coal chemist, technologist, or geologist, however, a treatise containing a summation of all known data bearing on the origin of coal would still leave much to be desired. Coal is a rock composed of different kinds of organic matter which vary in their proportions in different coals, and no two coals are absolutely identical in nature, composition, or origin.

The aim of this discussion is to present a summary of such knowledge of the origin of coal as is available in the literature. The literature is extensive, and it would be virtually impossible to discuss all publications on the subject. In addition to the articles primarily concerned with the origin of coal, many others present data that bear directly on related phases of the subject. It is probable that some articles that contain important contributions to our knowledge of coal have been overlooked by the author, but it is hoped that they will be considered by the authors of other sections of this volume more directly

related to the special fields to which those articles belong. The reader should remember that any summary, such as this, prepared from the literature, is likely to be influenced strongly by the background and experience of the compiler, which in this case is that of a geologist. With this in mind, attention is called to the papers on coal written by several authors¹ who have

¹ Stevenson, J. J., *Proc. Am. Phil. Soc.*, **50**, 1-116, 519-643 (1911), **51**, 423-53 (1912), **52**, 81-162 (1913). White, D., and Thiessen, R., *U. S. Bur. Mines, Bull.* **38** (1913), 390 pp. Stutzer, O., *Kohle: allgemeine Kohlengologie*, Gebrüder Borntraeger, Berlin, 1914, 2nd ed., 1923, 510 pp.; also published as a translation and revision by A. C. Noé, *Geology of Coal*, Univ. Chicago Press, 1940, 461 pp. Stopes, M. C., and Wheeler, R. V., "Constitution of Coal," *Dept. Sci. Ind. Research (Brit.) Monograph*, London, 1918, 58 pp. White, D., "The Carbonaceous Sediments" in *Treatise on Sedimentation*, Williams and Wilkins Co., Baltimore, 1926, pp. 266-316. Fuchs, W., *Die Chemie der Kohle*, Julius Springer, Berlin, 1931, 510 pp. Hickling, H. G. A., *Proc. S. Wales Inst. Engrs.*, **46**, 911-51 (1931); *Fuel*, **10**, 212-32 (1931). Duparque, A., "Structure microscopique des charbons du Bassin Houiller du Nord et du Pas-de-Calais," *Mém. soc. géol. Nord.*, **11**, No. 1 text, 547 pp., No. 2, plates, 1933. Stach, E., *Lehrbuch der Kohlen Petrographie*, Gebrüder Borntraeger, Berlin, 1935, 293 pp. Bone, W. A., and Himus, G. W., *Coal: Its Constitution and Uses*, Longmans, Green and Co., London, New York, Toronto, 1936, 631 pp. Thiessen, R., *Proc. Fuel Engrs. Conf. Appalachian Coals, Inc.*, **4**, 211-79 (1936-7); **5**, 112-75 (1937-8). Gothan, W., *Kohle*, Ferdinand Enke, Stuttgart, 1937, 432 pp. Moore, E. S., *Coal*, John Wiley & Sons, New York, 2nd ed., 1940, 473 pp.

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THE ORIGIN OF COAL

drawn heavily on the literature and present the subject from many points of view.

For the purposes of this discussion the definition of coal proposed by Stopes and Wheeler¹ and modified in accordance with a suggestion by Fox² is used. The definition is as follows: *Coal is a compact stratified mass of metamorphosed plants which have in part suffered arrested decay to varying degrees of completeness.* This definition excludes the various oil shales, canneloid shales, and carbonaceous shales, all of which are deposits in which inorganic material is dominant, and also excludes isolated coalified material such as stems, pinules, and fronds. The definition does include the following: brown coal, lignite, subbituminous, bituminous, and anthracitic coal; and boghead, cannel, pseudocannel, and splint coal. There is some doubt whether or not this definition includes peat. It would seem that peat is excluded as not metamorphosed. However, peat is considered the parent material from which humic coals are formed and will be treated as such.

EARLY THEORIES OF ORIGIN OF COAL

Peat Swamp or Autochthonous Theory. Thiessen,¹ Moore,¹ and others have pointed out that as early as the latter part of the eighteenth century von Beroldingen³ and Deluc³ believed that coal was formed from plant debris that had accumulated in a peat swamp, had been covered by later sediments, and had undergone later changes that produced a sequence of coals

beginning with peat and terminating with anthracite.

These ideas have been confirmed for most normal banded coals by the studies of later workers and may thus be said to constitute the first step in the development of our knowledge of coal. Among the more vigorous arguments in favor of autochthonous or *in situ* origin of coal-forming materials are those of Rogers,⁴ Potonié,⁴ and White.¹ A summary of their arguments is as follows: (1) The generally low content of mineral matter in coal precludes large-scale transportation of the plant material, as such transportation would have been accompanied by transportation of equally great amounts of mineral matter; (2) the presence beneath most normal banded coals of underclays, which are believed to be ancient soils, indicates growth of the plants *in situ*; (3) the wide lateral extent of many coal beds could have developed only in areas of essentially coextensive plant growth; (4) the arrangement and condition of the plant particles are not those of transported material; (5) the presence of rooted tree trunks and roots both in underclays and coals indicates plant growth *in situ*; (6) large modern peat deposits have formed *in situ*, cover comparatively large areas, and if converted to coal would form deposits comparable in size, shape, and purity to many coals; and (7) the deposition of the large quantities of plant debris in open water would leave the deposits subject to destructive bacterial decay.

Rogers⁴ in particular emphasized the widespread association of underclays with coals and interpreted them as ancient soils on which the dense vegetation of broad

² Fox, C. S., *Fuel*, 9, 548-59 (1930).

³ Von Beroldingen, F., *Beobachtungen, Zweifel, und Fragen, die Mineralogie überhaupt, und insbesondere ein natürliches Mineral-System betreffend*, Hannover, 1st ed., 1778, 203 pp., 2nd ed., 1792, vol. 1. Deluc, J. A., *Lettres, physique et morales sur les montagnes et sur l'histoire de la terre et de l'homme*, vol. 5, 1779, pp. 213-25; *J. physique*, 38, 174 (1798).

⁴ Rogers, H. D., *Repts. Am. Assoc. Geologists and Naturalists*, 71, 434-67 (1843); *Am. J. Sci.*, 43, 178-9 (1842). Potonié, H., *Die Entstehung der Steinkohle und der Kaustobiolithe*, Gebrüder Borntraeger, Berlin, 5th ed., 1910, 225 pp.

VARIOUS ALLOCHTHONOUS OR TRANSPORTATION THEORIES

coastal swamps grew. He cited Mammatt⁵ as first having called attention to the fact that an underclay generally accompanies a bed of coal. Mammatt believed that the clay particles and plant debris were mixed together in water and were separated into coal and its underlying clay by differences in settling velocities of the two materials. Rogers by emphasizing the soil nature of the underclays made perhaps the greatest stride toward establishing the idea that most common banded coals were formed at or near the place of plant growth. The soil nature of underclays has been accepted by most later workers, but Grim⁶ showed that underclays differ in profile from normal soils. Gresley⁷ likewise opposed the idea that underclays are soils and cited as supporting evidence the calcareous nature and absence of stigmariæ at many places in the underclay of the Pittsburgh coal as well as the absence of stigmariæ in very extensive shale partings in the coal.

Various Allochthonous or Transportation Theories. Throughout most of the nineteenth century many geologists, botanists, and chemists contended that the parent material of coal was not formed by degradation of plant material in place in peat swamps but rather resulted from the deposition of transported plant material in lakes, seas, and estuaries. One of the early theories was that of Hutton,⁸ who believed that particles of soot from smoke, soluble organic matter carried by streams,

and remains of plants and animals both native to the sea and transported from land were deposited in the sea, buried by inorganic debris, and later converted to coal.

The ideas of von Beroldingen⁹ and Deluc⁹ were attacked vigorously by Voight,⁹ who believed that coal was formed from the hardier reeds and through a process of solution of the vegetable debris in an oily substance later to be converted to coal. The peats and brown coals, however, did not pass through this process, according to Voight, and consequently do not constitute part of a series with coal. The coals of bituminous and higher rank were believed to be confined to Paleozoic strata, and peats and lignites to younger strata. These ideas influenced later thought to a considerable degree and did much to discredit the peat-swamp theory of the origin of the parent material of coal as well as the idea that coals form a definite series from peat to anthracite. As late as 1922, Donath and Lissner,¹⁰ for reasons unrelated to those of Voight, reiterated the opinion that peat and lignite are formed from plant materials that differ from those that form bituminous and anthracite coals. Their conclusions were based on differences in the nature of extracts from coals, lignites, and peats obtained with various reagents.

Von Leonhard¹¹ in 1835 argued strongly in favor of marine deposition of the parent material of coal. Fifty years later,

⁵ Mammatt, E., *Coal Field of Ashby de la Zouche*, W. Hextall and G. Lawford, London, 1834, pp. 71-4.

⁶ Grim, R. E., *Bull. Am. Ceramic Soc.*, **14**, 113-19, 129-34, 170-6 (1935).

⁷ Gresley, W. S., *Am. Geologist*, **14**, 356-65 (1894).

⁸ Hutton, J., *Theory of the Earth with Proofs and Illustrations*, Codell, Jr., & Davies, London, and W. Creech, Edinburgh, 1795, vol. 1, pp. 565-86.

⁹ Voight, J. K. W., *Versuch einer Geschichte der Steinkohlen, der Braunkohlen, und des Torfes*, Hoffmannsche Hof-buchhandlung, Weimar, 1802, vol. 1, 307 pp.

¹⁰ Donath, E., and Lissner, A., *Brennstoff-Chem.*, **3**, 231-7 (1922).

¹¹ Von Leonhard, K. C., *Lehrbuch der Geognosie und Geologie*, Schweizerbart, Stuttgart, 1835, 869 pp.

THE ORIGIN OF COAL

Fayol¹² proposed a theory of the formation of some of the coal beds of the Commeny basin by the segregation of plant debris as the lighter fractions of sediments of streams flowing into deltaic areas. According to Fayol, the lighter plant fragments were floated to the outer basins around deltas where they were deposited as organic concentrations that later were transformed to coal. Other proponents of various allochthonous theories were numerous up to 1900, when Grand'Eury¹³ proposed a theory of transportation of plant debris for short distances, from areas of growth on the margins to areas of deposition in the centers of restricted basins of open clear water. Since 1900, however, few if any students of coal have believed that any extensive coal deposits originated from transported debris; nevertheless, the theory was discussed by various authors as still worthy of consideration, and in 1911 was discussed exhaustively by Stevenson¹ before he felt free to accept evidence of the formation of coals from peats deposited *in situ*. In recent years, Jeffrey¹⁴ has stood practically alone in favoring an allochthonous origin for coals in general.

There is little doubt that some coals have been formed from transported materials. Even the stronger proponents of an autochthonous origin for the parent materials of normal banded coals recognize the fact that some coals such as cannel and bogheads are not the product of peat-swamp deposits. It is also certain that some banded coals have also been formed from transported materials. Such coals are generally somewhat unusual in that

they contain exceptionally abundant mineral matter or they are of limited extent.

Early Studies of Plant Structures in Coal. Prominent advances in the knowledge of the nature and origin of coal were made about fifty years after the work of von Beroldingen and Duluc from data supplied by microscopic studies of coal by Witham, Hutton, Reade, Link,¹⁵ and others, culminating for that time in the very comprehensive work of Goeppert.¹⁶ The principal value of that work was to yield many data on the kind of plants and types of plant structures preserved in coal.

Dawson,¹⁷ writing in 1871, attributed to Morris in 1840 and Fleming even earlier the correct recognition of spores in coal. Dawson found spores in many coals and canneloid shales and correctly interpreted the open-water conditions of deposition that gave rise to the concentration of spores in cannel coals.

Von Gümbel¹⁸ in 1883 prepared a treatise on the microscopic investigation of coal that may be said to represent the end of the early period of the study of coal. Von Gümbel summarized the available data and made logical generalizations. He showed that coals were formed in swamps from the debris of native land plants, the interstices of which were filled by a substance called "carbohumins" which was first introduced as a solution and later was

¹² Fayol, H., *Bull. soc. géol. France*, [3] 16, 968-78 (1887).

¹³ Grand'Eury, F. C., *Compt. rend. VIII^{me} congrès géol. intern., Paris*, 1901, pp. 521-38.

¹⁴ Jeffrey, E. C., *J. Geol.*, 23, 218-30 (1915); *Mem. Am. Acad. Arts Sci.*, 15, No. 1 (1924), 52 pp.

¹⁵ Witham, T. M., *On the Internal Structure of Fossil Vegetables Found in the Carboniferous and Oolitic Deposits of Great Britain*, Black, Edinburgh, 1833, 84 pp. Hutton, W., *London, Edinburgh, Dublin Phil. Mag.*, 2, 302-4 (1833); *Proc. Geol. Soc. London*, 1, 415-7 (1834). Reade, J. B., *Phil. Mag.*, 11, 13-7, 413-7 (1837). Link, F., *Abhandl. kgl. Preuss. Akad. Wiss. Berlin*, 1838, pp. 33-44.

¹⁶ Goeppert, H. R., *Haarlem Naturkund. Verhandl.*, [2] 4, 1-298 (1848).

¹⁷ Dawson, J. W., *Am. J. Sci.*, [3] 1, 256-63 (1871).

¹⁸ Von Gümbel, C. W., *Sitzber. math. physik. Klasse Akad. Wiss. München*, 13, 111-216 (1883).

TYPES OF COAL AND THEIR ORIGIN

fixed as a precipitate, so that the ground mass appears amorphous. The humin-like substances were believed to have been derived from the plant debris by slow decomposition without either great heat or pressure. Von Gümbel realized that coals were formed from various plant substances and under varying conditions both at the time of deposition and during the process of transformation from peat. Those variations in original materials, in their stage of decay and the external conditions of deposition, and in their geologic history after deposition as peat controlled the formation of different varieties of coals. Thus, von Gümbel outlined the theory of the formation of coals that is generally recognized today.

TYPES OF COAL AND THEIR ORIGIN

Normal Banded Coal. Most of the coals of the world may be described as normal banded coals. They are the coals made up of fine laminae and thicker bands of different types of coaly material. In general they consist of bands, laminae, and stringers of bright coal alternating with dull coal and fusain (mineral charcoal).

The prominent megascopic constituents of normal banded coal were considered as separate entities by Dawson¹⁹ as early as 1859. He stated the belief that bright coal, dull coal, and fusain were formed from segregations of particular plant parts or related plant parts. The method of segregation of bark, which he believed formed bright coal, from wood, which yielded fusain, and from fine plant debris that formed dull coal was not explained. Dawson did give a good description of the desiccation method of formation of mineral charcoal.

In 1881 Muck²⁰ published a study of coals in which he gave formal rank to the following terms that had long been in use as descriptive terms: Glanzkohle for bright coal, Mattkohle for dull coal, and Faserkohle for fusain or mineral charcoal. Although Muck apparently did little work on the various coal ingredients described, he did recognize the fact that they should be dealt with as distinctly different coal components.

A few years later a marked advance in the technique of coal research was made by Fayol²¹ in his study of the coals of Commentry. Fayol divided common banded coal into four ingredient parts which he studied separately. These were: bright bands or laminae (lames claires, miroitantes brillantes) similar to individual coalified trees, stems, branches, and trunks found in shales of the region; foliated coal (houille foliaire), constituted mainly of leaves and pollen grains and also containing fragments of debris of petioles, bark, etc.; granular coal (houille grenue) consisting of fine grains of plant debris unrecognizable to the naked eye; and fusain (zones mates, fusain) consisting of two varieties, one of which was silky and approached anthracite in composition, whereas the other was laminated and somewhat resembled bright coal. The bright coals contained plant structures visible under the microscope or even to the naked eye, were very low in ash (commonly less than 1 percent), and had the highest agglutinating value. The granular coal consisted of variable amounts of fragmentary leaf, petiole, bark, and pollen material, was homogeneous and resembled

²⁰ Muck, F., *Grundzüge und Zeile der Steinkohlenchemie*, Strauss, Bonn, 1881, 170 pp.; *Die Chemie der Steinkohle*, Wm. Engelmann, Leipzig, 1891, 284 pp.

²¹ Fayol, H., *Bull. soc. ind. minérale*, [2] 15, (1886), 543 pp.

¹⁹ Dawson, J. W., *Quart. J. Geol. Soc. London*, 15, 626-41 (1859).

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cannel, and belonged to the hard zones (zones ternes) of the coal. In some localities the granular coals graded into cannel or bogheads.

Fayol's approach to the detailed study of normal banded coal apparently made little impression on his contemporaries, and it remained for publication of independent studies of a similar nature by Stopes²² and Thiessen^{23, 24} in 1919 and 1920 to stimulate active research on coal ingredients. Each author introduced new names for bright and dull coals, but failed to define them clearly. The descriptions as given by the two authors differed somewhat, and there is an element of doubt as to what criteria defined each of their ingredients of coal.

The present status of nomenclature with the approximate correlation, though not absolute synonymy, between terms is shown in Table I. The important contribution

each type. The differences are so great that they necessitate the postulation of major differences in conditions in the early stages of the formation of the various parts of individual coal beds and of different beds.

Stopes's definitions were intended to apply to ingredients of coal visible to the naked eye and to be more or less independent of microscopic structure, although the microstructure of each ingredient was treated fully and was well illustrated by numerous photomicrographs. Thiessen's definitions, on the other hand, are based entirely on microscopic characteristics. Thus, according to their original definitions both sets of terms may be used helpfully in descriptions of a single coal.

Unfortunately, the terms used by Stopes have been confused by additional descriptions by both Stopes and later authors who have added microscopic characteris-

TABLE I
NOMENCLATURE OF COAL INGREDIENTS

Muck, 1881	Stopes, 1919	Thiessen, 1920	Fayol, 1886	General Meaning
Glanzkohle	Vitrain	Anthraxylon	Lames claires (miroitantes)	Glassy bright coal
	Clarain		Houille foliaire *	Striated bright coal
Mattkohle	Durain	Opaque atritus	Houille grenue *	Dull coal
Faserkohle	Fusain	Fusain	Fusain	Mineral charcoal

* Both belong to the "zones of hard coal" (houille ternes).

of the work of Stopes and Thiessen was to focus attention on characteristic differences between the coal in bright bands and dull bands, and even within the bands of

ties to the original descriptions. German workers have converted Stopes's terms to Vitrit, Clarit, Durit, and Fusit. Some, such as Winter,²⁵ have considered vitrain a material like dopplerite formed from the coagulation of a colloidal gel and devoid of plant structure. Others, like Robert

²² Stopes, M. C., *Proc. Roy. Soc. (London)*, **90B**, 470-87 (1919).

²³ Thiessen, R., *J. Geol.*, 1

²⁴ Thiessen, R., *U. S. Bu* (1920), 296 pp.

²⁵ Winter, H., *Glückauf*, **64**, 653-8 (1928).

CONDITION OF DEPOSITION OF THE PARENT MATERIALS

Potonié,²⁶ have suggested that terms such as "lignitoid Vitrit" for vitrain derived from wood, "suberitoid Vitrit" for vitrain derived from cork, and "Euvitrit" for vitrain without plant structure should be used. Duparque²⁷ described polished-surface preparations showing what he interpreted as all gradations from woody vitrain to "structureless" vitrain. For vitrain showing definite woody structure, he proposed the term "xylain," and for "structureless" vitrain, the term "xylovitrain." For vitrain in which all cavities are open but the cell-wall material has not developed the opacity characteristic of fusain, Stutzer²⁸ proposed the term "halb-fusit," and for similar material Hickling and Marshall²⁹ proposed the name "vitri-fusain." This passion for nomenclature has resulted in a heterogeneous mixture of terms that add conditions of formation, types of plant materials, and microscopic characteristics to the original megascopic descriptive terms of Stopes. Despite the confusion introduced with the terminology, much information concerning the nature of the ingredient materials of coals has been obtained.

Thiessen's³⁰ terms, anthraxylon and attritus, are based on megascopic appearance but are defined in terms of the nature and condition of the ingredient materials. Of anthraxylon, Thiessen said:

It is not difficult to show that the so-called bright coals are components that are derived from the woody parts of plants—

²⁶ Potonié, R., *Z. deut. geol. Ges.*, **78**, 357-80 (1926).

²⁷ Duparque, A., *Rev. ind. minérale*, **6**, part 1, 493-514 (1926).

²⁸ Stutzer, O., *Fusit*, Ferdinand Enke, Stuttgart, 1929, 139 pp.

²⁹ Hickling, H. G. A., and Marshall, C. E., *Trans. Inst. Mining Engrs. (London)*, **86**, 56-75 (1933).

³⁰ Thiessen, R., and Francis, W., *U. S. Bur. Mines, Tech. Paper 446*, 5, 11 (1929).

parts that at one time were largely composed of wood or woody tissues.

As it is derived from woody tissues (pieces of wood turned into coal) and consists of definite units easily distinguishable from the rest of the coal, it will be called anthraxylon, from the Greek *anthrax*, coal, and *xylon*, wood.

Attritus was defined as follows:

... dull coal consists largely of smaller anthraxylon constituents, together with a few other constituents such as cuticles and bark-like constituents, embedded in a general matrix, the attritus.

At low magnification the attritus appears as a uniformly granular, amorphous mass. ... A close examination at high magnification will at once reveal ... woody degradation products or humic matter, spore-exines, resinous matter, cuticular matter, more highly carbonized matter, certain small bodies usually designated as rodlets or needles, and some mineral matter.

It is apparent from some later papers that Thiessen³¹ considered anthraxylon anything in coal (other than fusain) that shows distinguishable cell structure and occurs as a coarse constituent, and that he did not confine anthraxylon to coarse wood only, but included in it bark, pith, and even nonwoody hydrophytic plants.

Condition of Deposition of the Parent Materials. The normal banded coals are generally believed to have formed from peat-swamp types of deposits. Potonié⁴ divided the coal-forming materials into three groups: humic coals, sapropeliths, and liptobioliths. He believed that the parent material of humic coal was formed by the partial decay of land plants and swamp plants in a moderately moist habitat. Such coal is bright coal or Glanzkohle rich in carbohydrates. The sapropeliths were formed in stagnant water from the remains of aquatic organisms that

³¹ Thiessen, R., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 573*, 3-21 (1937).

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were primarily planktonic. The most important of these were the oil-bearing algae, certain crustaceans, and a subordinate admixture of pollen grains and other drifted materials. Liptobioliths consist primarily of resins, waxes, and spores and represent the more stable residue of decomposed land plants. Potonié explained the banding of normal coal by postulating alternation of moist conditions which yielded bright coal with periods of pronounced dryness that permitted more complete destruction of humic materials and the formation of dull bands of liptobiolithic materials and occasional periods of flooding that produced sapropels.

White¹ in 1913 discussed comprehensively the topographic and climatic conditions favoring the formation of peat swamps of the type necessary to have formed our known coal. Topographically, broad coastal swamps just above the tidal range, or broad inland base-level basins, were considered necessary. Climatically, even, tropical to subtropical, extremely humid conditions were believed to have prevailed.

Giles³² later advanced strong arguments against the interpretation of data bearing on the tropical to subtropical nature of climates during peat formation in Carboniferous time.

There can be little doubt that the conditions of deposition of coal-forming material must have been such as to prevent complete decay of the plant material. This may have been accomplished by either: (1) rapid burial beneath other sediments, which probably occurred in the cases of many isolated stems, fronds, pinnules, etc., that have been coalified; or (2) complete saturation of the plant debris or the existence of a water cover at the site of depo-

sition of the plant material. The function of water in retarding decay was twofold: (1) it inhibited free access of oxygen to the decay-producing micro-organisms; and (2) it served as a solvent for certain products of decay that were toxic to at least some of the micro-organisms.

The water cover obviously would be ineffective in arresting decay unless it were stagnant, because if either surface or subsurface drainage or any other form of circulation or influx and withdrawal, as by tidal action, occurred, the supply of oxygen would be replenished by the aerated water and the soluble toxic products would be in part removed by waters leaving the deposits and in part diluted by the influx of aerated water. Furthermore, the water must have been very shallow (no more than a few feet deep) in order to permit the growth of an adequate supply of plant material which also would have prevented aeration of the water through agitation by wind.

Stagnant shallow water exists under a number of different conditions, for example: (1) broad coastal swamps of such low relief that seaward migration of surface and ground water is slight; (2) similar broad swamps around inland basins or lakes; (3) shallow inland depressions underlain by impervious material, such as depressions in glaciated areas underlain by glacial clays; (4) shallow inland depressions in areas where the slope of the ground-water surface is too slight to permit subsurface drainage. Peats are known to have formed under all these conditions within comparatively recent time, and it is probable that the peats that have become our most extensive coal deposits were formed under similar conditions.

It is apparent that both surface and subsurface drainage³ must be retarded in order to establish an adequate peat marsh.

³² Giles, A. W., *Bull. Am. Assoc. Petroleum Geol.*, 14, 1279-99 (1930).

BIOCHEMICAL STAGE OF COAL FORMATION

The surface drainage is clearly a function of topography. Subsurface drainage is a function of both topography and the permeability of the underlying materials. It seems significant in this connection that most of the extensive coal beds rest upon underclays, and underclays have very low permeabilities.

It is obvious that, under the conditions of peat formation outlined above, land plants, hydrophytic plants, and purely aquatic plants like the algae may all have contributed to the organic debris. Practically all types of plants and all parts of plants have been recognized in coal by various workers. It is equally evident that the conditions of peat formation varied within certain limits. Variations in those conditions must have produced some variation in the nature of the peat that was formed, which in turn must have resulted in some variation in the nature of the coal to which the peat was converted. Renault,³³ Potonié,⁴ and White¹ showed that variations in the amount, toxicity, and aeration of the water could account for most of the variations in the nature of the ingredients of peat and coal.

Biochemical Stage of Coal Formation. White³⁴ in 1908 postulated two important stages in the formation of normal banded coals, the biochemical (or peat) stage and the dynamochemical (or metamorphic) stage. White's concept of the biochemical (or peat) stage in coal formation had much in common with ideas of Renault and Potonié. Renault³³ emphasized the importance of bacteria and fungi in the partial destruction of plant material to produce a "fundamental jelly" which he believed to be the matrix of coals in general. Potonié³⁵

called attention to the selective destruction of carbohydrates and the concentration of resins, waxes, and spores in the process of decay under conditions permitting aeration of accumulated humic debris. White's biochemical stage represents the period of alteration of plant debris to peat. In this stage, micro-organisms, particularly bacteria, attack the plant material until the absence of an adequate supply of oxygen or the development of exterminative toxins ends the microbial activity. If the process reaches an advanced stage, a mature black peat or even "amorphous" peat is formed. If the stage is less advanced, the peat contains more wood and other undecomposed matter and is brown. If the vegetable refuse falls into more nearly aseptic water where the decay is relatively little, the peat is lighter brown, fibrous, and distinctly xyloid. Alternations in these conditions and deposits produce the banding in normal banded coal.

In contrast to these ideas, Stadnikoff³⁶ has contended that the segregation of the materials that produce the various bands in coals is not original but is due to a process of filtration in the peat stage that results in the separation of a peat bed into layers.

Thiessen and Strickler³⁷ learned from studies of four peat swamps in Wisconsin that both aerobic and anaerobic bacteria were present to the full depth of the swamp, maximum of 9 feet. Actinomyces and fungi were present in the upper layers but were not found below a depth of 4 feet. The peats in general were slightly acid except in the surface layers and in one layer containing shells.

³³ Renault, B., *Bull. soc. ind. minérale*, [3] **13**, 865-1169 (1899).

³⁴ White, D., *Econ. Geol.*, **3**, 292-318 (1908).

³⁵ Potonié, H., *Abhandl. kgl. geol. Landesanstalt*, **19**, 1-94, especially 48 (1906).

³⁶ Stadnikoff, G., *Kolloid-Z.*, **57**, 221-5 (1931).

³⁷ Thiessen, R., and Strickler, H. S., *Carnegie Inst. Tech. Coop. Bull., Mining Met. Invest.*, **61** (1934), 19 pp.

Thiessen and Johnson³⁸ and Waksman and Purvis³⁹ have shown that micro-organisms, principally anaerobic bacteria, are present at all levels in peat deposits. Taylor⁴⁰ has published a series of articles presenting a theory of the formation of all ranks of coal up to and including anthracite by bacterial action under varying conditions. Taylor contended that peat was formed in an acid environment in deposits not covered by later sediments; lignite, in an acid environment under a roof containing calcium-bearing clay minerals; and higher-rank coals, under alkaline anaerobic conditions under a roof containing sodium-bearing clay minerals. The formation of anthracite or bituminous coal under the third set of conditions was controlled by the degree of decomposition reached in the peat stage. These ideas are so completely at variance with so many known facts concerning coals that they cannot be fitted into the generally held concepts of coal formation.

The order of decomposition of the various plant ingredients in the process of peat formation was discussed at length by Waksman and Stevens.⁴¹ The general order of decomposition of groups of compounds is: (1) protoplasm; (2) chlorophyll; (3) oils; (4) the carbohydrates: (a) starches, (b) celluloses, (c) lignins; (5) epidermis; (6) seed coats; (7) some pigments; (8) cuticles; (9) spore and pollen exines; (10) waxes; (11) resins. The first three disappear very early in the process of decay; the last four are very

resistant and are present long after the almost complete elimination of the other materials. The value of these data was recognized by White,⁴² who showed the significance of this orderly sequence of resistance to decay in peats destined to become banded coals. White showed that with this sequence the degree of toxicity of peat-swamp waters controlled the composition of the peat. In highly toxic waters such as would be found in a completely stagnant swamp, little decay would have occurred and the more resistant materials up to and including the celluloses and hemicelluloses would be preserved (line A-A, Fig. 1). In less toxic waters, the celluloses would be destroyed and a peat would form that contained some hemicelluloses, the lignins, and the hydrogenous materials (line B-B, Fig. 1). In better-aerated water, the hemicelluloses would disappear and leave only lignins and hydrogenous constituents (line C-C, Fig. 1). In well-oxygenated water, lignin likewise would disappear (line D-D, Fig. 1). Any influx of aerated water would accelerate bacterial decay by dilution of the toxic compounds. Highly toxic waters that inhibit decay would result in the preservation of most of the plant materials in large pieces in a peat which would later be converted to the "anthraxylon" of Thiessen and the "vitrain" of Stopes. Less toxic conditions permitting the destruction of most of the celluloses and hemicelluloses would result in fragmentation of large plant debris and the concentration of lignins, epidermis, cuticles, spores, waxes, and resins, and would yield a mature peat destined to become the "clarain" of Stopes. In better-aerated waters permitting even more decay, the plant fragments would be broken down to a micro-debris rich in lig-

³⁸ Thiessen, R., and Johnson, R. C., *Ind. Eng. Chem., Anal. Ed.*, **1**, 216-28 (1929).

³⁹ Waksman, S. A., and Purvis, E. R., *Soil Sci.*, **34**, 95-113 (1932).

⁴⁰ Taylor, E. M., *Fuel*, **5**, 195-202 (1926), **6**, 359-67 (1927), **7**, 66-71, 127-8, 129-30, 180-4, 227-8, 228-9, 230-8 (1928).

⁴¹ Waksman, S. A., and Stevens, K. R., *Soil Sci.*, **26**, 113-37, 239-51 (1928). Waksman, S. A., *Brennstoff-Chem.*, **13**, 241-7 (1932).

⁴² White, D., *Econ. Geol.*, **28**, 556-70 (1933).

nins, spores, cuticles, waxes, and resins which would be the parent material of Thiessen's "attritus" and the "durain" of Stopes. In well-oxygenated waters the spores, cuticles, resins, and waxes alone would accumulate as the peat equivalent of canneloid coal, probably pseudocannel.

The Lignin versus Cellulose Discussion. For many years it was assumed by most workers that cellulose was the principal plant compound that contributed to coal formation. However, in 1921, Fischer and Schrader⁴³ published some conclusions concerning the chemical constituents of plants that constitute the parent materials of humic coals. The conclusions were based largely on chemical studies of coals, cellulose, and lignin. Fischer and Schrader concluded that in peat formation cellulose is easily decomposed to carbon dioxide and water by the action of micro-organisms and consequently plays no important part in coal formation. Lignin is more resistant to bacterial action, is concentrated in the residue, and is easily converted to humins and humic acid, whereas resins and waxes are transformed to bitumens. Fuchs⁴⁴ and Marcusson⁴⁵ found that the bulk of brown coals consists of humic acids and humates. Fuchs¹ and Stadnikoff⁴⁶ with some modification concur with the general lignin theory of the origin of humic coals.

Trussow⁴⁷ had shown that cellulose does not yield humic acids but that lignin, proteins, tannins, and fats do. Marcusson⁴⁸ contended that in the change from wood

to peat to brown coal the content of lignin remains essentially constant whereas the cellulose content decreases by alteration to oxycellulose and pectins from which humic acids are derived. Waksman and his associates^{41, 49} have stated that micro-organisms, primarily bacteria, convert cellulose

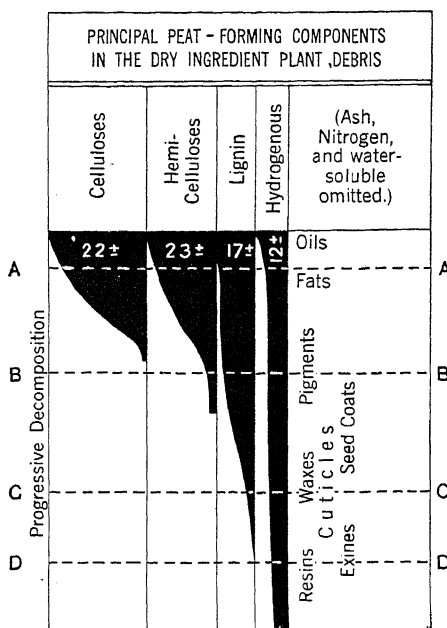


FIG. 1. Approximate proportions of principal peat-forming plant substances plotted according to relative resistance to microbial decomposition, and order of disappearance.⁴²

into their cell substances which in turn are converted to humus after their death. They concluded that the humic compounds are derived from two fundamental sources: (1) the resistant plant substances such as lignin, cuticles, resins, and waxes; and (2) compounds derived from synthetic cell substances formed by micro-organisms

⁴³ Fischer, F., and Schrader, H., *Brennstoff-Chem.*, **2**, 37-45 (1921).

⁴⁴ Fuchs, W., *Brennstoff-Chem.*, **8**, 337-40 (1927); also see pp. 169-71 of ref. 1.

⁴⁵ Marcusson, J., *Z. angew. Chem.*, **40**, 1104-6 (1927).

⁴⁶ Stadnikoff, G., *Die Chemie der Kohlen*, Ferdinand Enke, Stuttgart, 1931, 339 pp.

⁴⁷ Trussow, A. G., *Contributions to the Study of Russian Soils*, Petrograd, 1917, pp. 26-7.

⁴⁸ Marcusson, J., *Z. angew. Chem.*, **39**, 893-900 (1926), **40**, 48-50 (1927).

⁴⁹ Waksman, S. A., and Skinner, C. E., *J. Bact.*, **12**, 57-84 (1926). Waksman, S. A., *Cellulosechem.*, **8**, 97-104 (1927). Waksman, S. A., *Humus*, Williams and Wilkins Co., Baltimore, 1936, 494 pp.

from cellulose, pentosans, starch, sugar, and proteins. Waksman further concluded that humus collects only at relatively low temperatures under anaerobic and acid conditions, as otherwise the processes of decay continue until all the materials are destroyed.

Terres⁵⁰ contended that proteins are essential materials for the formation of bitumens. This conclusion was based on experiments with fermented proteins heated in an autoclave at 200 to 300° C in which a heavy oil was obtained. Terres considered such oil the parent material for bitumen and an essential ingredient of coking coals.

Bergius⁵¹ heated lignin and cellulose to approximately 340° C in the presence of water and under high pressure and succeeded in producing a substance that he believed to resemble bituminous coal. He concluded from those experiments that coal can be formed directly from lignin and cellulose by chemical reaction at high temperatures over a short time or at low temperatures under reasonable pressure and over a long period of time. He did not consider bacterial action essential to this process.

Berl and his associates⁵² have also produced coal-like materials at high pressure, temperatures of 200 to 350° C, and in the presence of alkalis. The general conclusions drawn from their work were that both cellulose and lignin contribute to coal formation, cellulose predominating in coals with high bitumen content and good coking properties and lignin predominating in the noncoking coals.

⁵⁰ Terres, E., *Proc. 3rd. Intern. Conf. Bituminous Coal*, **2**, 797-808 (1931).

⁵¹ Bergius, F., *Naturwissenschaften*, **16**, 1-11 (1928).

⁵² Berl, E., and Schmidt, A., *Ann.*, **493**, 97-152 (1932). Berl, E., and Keller, H., *Ann.*, **501**, 84-106 (1933).

Yasui⁵³ studied the optical properties of the cell walls in plants, lignites, and bituminous coals and concluded that cellulose disappears comparatively early in the process of coalification, as indicated by the progressive decrease of the double refraction characteristic of cellulose as the rank of the coal increases.

One must conclude from the data supplied by these various lines of research that all plant materials contribute to the formation of coal, as must also the remains of micro-organisms that have accomplished the partial decay of the original plant materials. The nature of the original materials, the degree of decay of those materials, and the amounts of soluble derivatives that remain in the peat must control the type of the coal formed, but no single set of conditions need prevail for the formation of coal. Although lignin may be the principal component of peat and humus and consequently the principal parent material of coal from a chemical point of view as believed by Fischer and Schrader,⁴⁸ Fuchs,¹ and others, there can be little doubt that cellulose, proteins, and other compounds contribute at least a part of the total coal-forming material. The contribution of these compounds may be in large measure made indirectly through degradation products.

Colloidal Chemical Stage. In 1908, Campbell⁵⁴ called attention to an interesting characteristic of lignite and sub-bituminous coals—the tendency to slack when dried. This suggested that at least some of the water in low-rank coal is an integral part of the coal structure and not merely extraneous material. Mack and

⁵³ Yasui, K., *Bot. Mag. Tokyo*, **39**, 280-9, 289-97 (1925); *Japan J. Geol.*, **8**, Abstract sect. 9 (1930); *Chem. Abs.*, **25**, 3277-8 (1931).

⁵⁴ Campbell, M. R., *Econ. Geol.*, **3**, 134-42 (1908).

Hulett⁵⁵ later suggested that compact peat is essentially a hydrosol which through slow alteration processes becomes a hydrogel in low-rank coal. Gauger⁵⁶ concluded from experiments dealing with the accuracy of water determinations in low-rank coals that peat has the properties of a hydrosol and lignite those of a hydrogel that has a spongelike structure with ultra-microscopic capillaries of varying radii. Stach⁵⁷ expanded this concept to that of a colloid chemical stage in the formation of coal. In the peat-forming stage of coal formation, plant materials are converted to humic acids and combined water. In the succeeding colloidal chemical stage (late peat-lignite), humic acid gels are aged in the presence of water to form alkali-insoluble humic compounds. These compounds constitute the impregnating materials in the more woody parts of the coals. The tendency of the colloidal material to concentrate in capillaries is illustrated by experiments bearing on the precipitation of humic colloids in soil, cited by Kubiěna.⁵⁸ Coatings of humic colloids were formed in interangular areas of mineral grains and in capillaries. Grains were also coated by a process of creeping in capillaries of precipitated colloidal material across the surface of the grain. Lavine⁵⁹ emphasized the colloidal characteristics of lignites and subbituminous coals by calling attention to the hysteresis in alternate wetting and drying, to their behavior in response to an electric current, to their absorption properties, and to their peptization by treatment with

alkaline solutions, all of which were considered definite indications of colloidal nature.

Tideswell and Wheeler⁶⁰ in a discussion of dopplerite in peats concluded that dopplerite is a gel composed of ulmins derived from plant carbohydrates either directly by bacterial action or by chemical reactions between carbohydrates and amino acids produced by bacterial destruction of proteins. It was also suggested that dopplerite is the material that has impregnated vitrain and with later alteration has produced the bright luster and conchoidal fracture of vitrain. It is further possible that altered dopplerite may constitute the parent material of "structureless" vitrain.

It seems probable that this stage of development of colloids in the late peat stage followed by the fixation of the colloidal organic material through the elimination of water in the lignite and early subbituminous stages may constitute the really important change in the conversion of peat to coal. Consideration of this stage also suggests that a possible difference between true lignites and at least some of the brown coals may lie in differences in the amount of colloidal material concentrated in the parent peats of each. Many brown coals are poorly consolidated and are difficult to distinguish from peat. It appears possible that this may be due either to the failure of colloids to develop or to the escape of developed colloids and the consequent absence of impregnation of the peat by colloidal organic material.

Marshall⁶¹ has published excellent studies of a number of vitrains in which he describes shrinkage of the inner cell sacs

⁵⁵ Mack, E., and Hulett, G. A., *Am. J. Sci.*, [4] **43**, 89-110 (1917).

⁵⁶ Gauger, A. W., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 148-61 (1932).

⁵⁷ Stach, H., *Braunkohlenarch.*, **40**, 1-51 (1933).

⁵⁸ Kubiěna, W. L., *Micropedology*, Collegiate Press, Ames, Iowa, 1938, pp. 132-35.

⁵⁹ Lavine, I., *Ind. Eng. Chem.*, **26**, 154-64 (1934).

⁶⁰ Tideswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **121**, 2345-62 (1922).

⁶¹ Marshall, C. E., *Fuel*, **20**, 52-9, 82-91 (1941).

in woody material and apparent impregnation of the resultant capillaries by colloidal organic matter. It appears possible that one explanation of some of the differences between vitrain and clarain on the one hand and durain on the other may lie in their relative suitabilities as hosts and entrapping media for organic colloids. The greater decay of material destined to form durain may have so enlarged the capillaries and increased the porosity of the residue as to permit the escape of organic colloids and their concentration in the finer capillaries of less decomposed bands later to become vitrain or clarain.

Dynamochemical or Metamorphic Stage.

As soon as peat is buried by later sediments, it is subjected to pressure by the load of overburden, and from that time onward through its history the organic residue is undergoing changes in response to the two agencies of heat and pressure. It is apparent that just as the colloidal chemical stage of coal formation overlaps with the peat stage so does the metamorphic stage overlap with both the early stages.

The first of these agencies active in the alteration of organic residues is almost certainly pressure from the weight of overburden. Hilt⁶² as early as 1873 stated that the fixed-carbon content of coals increases progressively with increased depth of burial. It was Hilt's opinion that depth of burial was the principal agency in effecting the increase in rank of coals from lignite to anthracite. Strahan and Pollard⁶³ found, from a detailed study of the anthracites and bituminous coals of Wales, that in a single shaft encountering several coal beds

the deeper coals in general had the higher fixed-carbon contents. However, that rule was not constant, and in considering the horizontal extent of the coals it was found that those of higher fixed-carbon content were present in areas where the total thickness of overburden had been least. Thus, their studies indicated that depth of burial was a factor in coal metamorphism but demonstrated clearly that depth of burial was not the sole factor. Strahan and Pollard concluded that difference in composition of original materials was the largest single factor in determining the variations in fixed-carbon content in coals in that field.

Ashley⁶⁴ in a study of cannel coals found that, in coals of low rank, cannels contained much less fixed carbon than closely associated normal banded coals because of the differences in original materials. Analyses cited by Ashley, however, show that, when woody coal has been subjected to sufficient metamorphism to raise the fixed-carbon content to as much as 75 percent (dry, ash-free), canneloid benches of the same bed contain about the same amount of fixed carbon as the woody coal. It is apparent from these studies that factors other than depth of burial and nature of the original materials must also influence the rank of a coal.

White^{65, 66} has developed the thesis that horizontal thrust pressure due to deformation of the earth's crust is the dominant agency in effecting the metamorphism and increase in rank of coal. White considered vertical pressure from overburden effective in the early stages of increase in

⁶² Hilt, C., *Z. Ver. deut. Ing.*, **17**, 194-202 (1873).

⁶³ Strahan, A., and Pollard, W., "The Coals of South Wales, with Special Reference to the Origin and Distribution of Anthracite," *Geol. Survey Gt. Brit., Mem. Geol. Survey England and Wales*, 1908, 78 pp.

⁶⁴ Ashley, G. H., *U. S. Geol. Survey, Bull.* **659**, 17 (1918).

⁶⁵ White, D., *J. Washington Acad. Sci.*, **5**; 189-212 (1915); *Bull. Am. Assoc. Petroleum Geol.*, **19**, 589-617 (1935).

⁶⁶ White, D., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 253-81 (1925).

rank of coal but believed it to be merely a controlling factor as resistance to thrust pressures in the more advanced stages of metamorphism of coal. He realized that the increase in rank of coal under the influence of thrust pressure was the result of a combination of the direct effect of pressure with increased temperature resulting from compression and friction induced by the pressure, both agencies operating over a long time period.

Many geologists, especially among the Americans and Canadians, accept the accuracy of White's conclusions, although some geologists⁶⁷ have suggested that factors such as weight of overburden, variations in original materials and the nature of enclosing strata, and heat from other sources may have influenced the increase in rank of coals to a greater degree than was supposed by White. The attempt to explain nearly all variations in rank of coal by variations in thrust pressure led White⁶⁶ and later Hendricks⁶⁸ into somewhat strained arguments concerning the distribution of forces in thrust pressures in the Arkansas-Oklahoma coal field, where anomalous relationships exist between the degree of deformation and the variations in carbon ratios. Fisher⁶⁷ in a discussion of the last-cited paper called attention to "the possibility of hydrothermal activity entering into this picture."

Some data and opinions have been presented on the temperatures to which coals of various ranks have been subjected. Wheeler and his associates⁶⁹ have made

studies of the thermal decomposition of coal in a vacuum. They found that the decomposition points of the lignites that were studied ranged from 225 to 290° C, that no marked decomposition of any bituminous coal occurred below 300° C, and that rapid decomposition of bituminous coals occurred at 310 to 320° C. They believed that the gases and liquids that appeared at lower temperatures were yielded by free hydrocarbons and did not represent decomposition products. These data should not be expected to indicate limiting temperatures to which the coals could have been subjected because they do not take into account the possible effect of pressure in modifying the influence of heat on the coals.

Many workers have presented experimental data bearing on the temperatures necessary to produce changes in rank of coal. Erdmann⁷⁰ concluded from the conversion of lignite to bituminous coal by heating at 260° C under 70–80 atmospheres of pressure that increased temperatures and pressures are essential to the formation of bituminous coal. Similar results and conclusions resulted from experiments of Gropp and Bode⁷¹ which indicated that the degree of alteration of a coal was a direct function of the temperature to which it had been subjected. From studies of anthracites and semicokes, Roberts⁷² concluded that the two were so similar that anthracite must be formed at practically the same temperature as semicoke, which is from 500 to 550° C. Lewis⁷³ found that heating a low-rank coal under

⁶⁷ Dorsey, G. E., *Bull. Am. Assoc. Petroleum Geol.*, **11**, 455–65 (1927). Russell, W. L., *ibid.*, **11**, 977–89 (1927). Reeves, F., *ibid.*, **12**, 795–823 (1928). Fisher, D. J., *ibid.*, **20**, 102–6 (1936).

⁶⁸ Hendricks, T. A., *ibid.*, **19**, 937–47 (1935).

⁶⁹ Holroyd, R., and Wheeler, R. V., *J. Chem. Soc.*, **1928**, 3197–203. Wheeler, R. V., and Vernon, W. L., *ibid.*, **1930**, 1819–28. Ashmore, J. E., and Wheeler, R. V., *ibid.*, **1934**, 474–80.

⁷⁰ Erdmann, E., *Brennstoff-Chem.*, **5**, 177–86 (1924).

⁷¹ Gropp, W., and Bode, H., *Braunkohle*, **31**, 277–84, 299–302, 309–13 (1932).

⁷² Roberts, J., *Proc. S. Wales Inst. Engrs.*, **40**, 97–138 (1924).

⁷³ Lewis, E., *Colliery Guardian*, **152**, 1147–9, 1199–201 (1936).

a pressure of 300 pounds per square inch produced hydrogen and oxygen losses practically identical with those of a series of coals of increasing rank. Up to 550°, the loss of oxygen exceeded that of hydrogen, but above 550° the evolution of oxygen decreased and became less than that of hydrogen. According to White,⁷⁴ the loss of oxygen is more rapid than that of hydrogen with increasing rank through the bituminous coals, but it is at about the same rate in the passage on to anthracite. Dapples⁷⁴ has called attention to the presence in bituminous coals of the Anthracite-Crested Butte area, Colorado, of waxes that melt from 193 to 210° C under atmospheric pressure. No resins or waxes are present in the anthracites of the area, although cavities of the size and shape of those containing resins in bituminous coal were found to be filled with mineral matter. This area is one in which heat from igneous intrusives has played an important part in the formation of the anthracite. White⁷⁵ described the occurrence of resins in numerous Paleozoic and younger coals of low rank (lignite, subbituminous, and high- and medium-volatile bituminous) and called attention to their absence in high-rank coals. With increase in rank of the coals the resins first darken, shrink and crack, then become brownish black, spongy or granular, residues, and still later are reduced to a thin, fine, black, powdery scale. This behavior of the resins in the coals is suggestive of the action of resins when heated, as pointed out by Dapples.⁷⁶

It is interesting to note that, in the highest-rank coals in which resin was observed by White, it occurred as darkened

and shrunken rodlets in fusain, but the very brittle and easily crushed fusain was not crushed. This suggests that the alteration of the resins resulted largely from increased temperature rather than increased pressure, to which White^{65, 66} later ascribed so dominant a role. Turner⁷⁷ has shown that fusain is a common constituent of anthracite, in which it exists as uncrushed particles with open pores and of such fragility that it must be boiled in balsam and xylol before thin sections can be cut. Turner also called attention to the presence of powdery black material in some of the pores. This description is very similar to White's description of the final condition of resins in high-rank coals.

Stadnichenko and White⁷⁸ later showed that spores, algae, resins, and waxes, in the presence of inert gases, melt and volatilize at temperatures less than 500° C. Zetzsche and Kälin⁷⁹ isolated spores and pollens from bituminous coal and heated them at 140 to 340° C with water, glycerol, or paraffin under pressure. The spores and pollens were partly decomposed by this treatment, and the authors concluded that the absence of evidence of similar decomposition of spores and pollens in bituminous coal shows that those coals were never subjected to temperatures greater than 200° C.

Neumann⁸⁰ concluded from the stages of alteration of resins that ordinary brown coals were formed at temperatures of 150–180°, some bright brown coals at 265–320°, and some low-rank bituminous coals at 230–300° C. Kirchheimer⁸¹ studied

⁷⁷ Turner, H. G., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 127–41 (1925).

⁷⁸ Stadnichenko, T., and White, D., *Bull. Am. Assoc. Petroleum Geol.*, **10**, 860–76 (1926). Stadnichenko, T., *ibid.*, **13**, 823–48 (1929).

⁷⁹ Zetzsche, F., and Kälin, O., *Helv. Chim. Acta*, **15**, 670–4, 675–80 (1932).

⁸⁰ Neumann, B., *Brennstoff-Chem.*, **15**, 25–7 (1934).

⁸¹ Kirchheimer, F., *ibid.*, **15**, 21–5 (1934).

⁷⁴ Dapples, E. C., *Econ. Geol.*, **34**, 309–98 (1939).

⁷⁵ White, D., *U. S. Geol. Survey, Professional Paper* **85**, 65–83 (1914).

⁷⁶ Dapples, E. C., *Trans. Illinois State Acad. Sci.*, **30**, 176–7 (1938).

thermal effects on pollens and spores and made comparisons with the condition of those materials in various low-rank coals. From those studies he concluded that the temperatures did not reach 130° in the formation of soft brown coals, that they were between 130 and 200° during the formation of the bright brown coals, and that they were above 200° C during the formation of low-rank bituminous coals.

Numerous examples of increase in rank of coal in zones near igneous intrusions have been described.⁸² In many such occurrences the common result is that either the coal is burned or coke is formed in contact with the igneous rock, anthracite is formed near but not in contact with the igneous rock, and the rank of the coal decreases at progressively greater distances from the intrusive. Among the papers that suggest definite temperatures at which changes in rank of coal occur as the result of igneous intrusions is that of McFarlane,⁸³ who studied coals of the Yampa coal field, Colorado, that have been altered by local igneous intrusives. McFarlane concluded that the changes from low-rank bituminous coal to semianthracite takes place in the range of temperature from 160 to 350° C, true anthracite is formed at temperatures between 350 and 600° C, and natural coke at temperatures between 600 and 900° C. Above 900° C the pores of the coke begin to close.

Briggs⁸⁴ has contended that time alone

is adequate to produce all the changes in rank of coal, although he has conceded that moderate heat and pressure accelerate the progressive changes. His idea is so inconsistent with the wide distribution of coals of the same age but of different ranks and also with the wide distribution of coals of vastly different ages but the same rank that the acceptance of time as the single important agency is impossible. Briggs⁸² also cited some pressure experiments conducted by J. Wilson in which peat, lignite, and several bituminous coals were subjected to pressures of 15 tons per square inch with relatively constant controlled temperature. The pressure was increased in 5-ton steps at 15-minute intervals and was held at 15 tons for one hour. Losses of volatile matter (dry, ash-free basis) were, for four samples: peat, 2.8 percent; lignite, 4.3 percent; and bituminous coal, 1.48 to 4.14 percent. These results show that pressure can reduce the volatile content of a coal, but the data are inadequate to show whether the volatile matter lost was merely occluded gas or was in part gas derived from solid compounds in the coal as a result of the pressure.

Campbell,⁸⁵ in discussing the progressive increase in rank of coal, which he attributed to pressure, stressed the development of a high degree of friability in coal of low-volatile bituminous rank and the recementation of the friable coal upon conversion to semianthracite. The most significant chemical changes in the coal in this stage of alteration are the acceleration in loss of hydrogen previously mentioned and a relative increase in the fixed-carbon content. The concurrence of these two phenomena is suggestive of a causal relationship between them. It seems probable that the recementation is accomplished by the poly-

⁸² Rogers, W. B., *Am. J. Sci.*, **43**, 175-6 (1842).
Clough, C. T., et al., "The Economic Geology of the Central Coal Field of Scotland. Area V. Glasgow East, Coatbridge, and Airdrie," *Geol. Survey Gt. Brit., Mem. Geol. Survey Scotland*, 1926, 171 pp. Eby, J. B., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 246-52 (1925). Briggs, H., *Trans. Inst. Mining Engrs.*, **89**, 187-219 (1935).
Marshall, C. E., *ibid.*, **91**, 235-60 (1936).

⁸³ McFarlane, G. C., *Econ. Geol.*, **24**, 1-14 (1929).

⁸⁴ Briggs, H., *Chemistry & Industry*, **50**, 127-33

⁸⁵ Campbell, M. R., *Econ. Geol.*, **25**, 675-96 (1930).

merization of some hydrocarbon compound or group of compounds that results in the loss of hydrogen and the cementation of the friable coal. To accomplish recementation the percentage of carbon must be increased in the crystal structure of materials present in the coal. The restriction of such cementation to a small part of the metamorphic sequence in coals suggests that it occurs only above a critical temperature or at elevated temperatures that may vary with varying pressure. Roberts⁸⁶ recognized the fracturing and recementation stages of coal metamorphism and attributed the recementation to carbonization and semifusion at about 500° C under pressure too great to permit the development of the porous structure of coke.

Some X-ray studies by Sedletskii⁸⁷ indicate that lignin, humic acid, and coal have crystal structures resembling graphite. His X-ray studies indicated that the size of the crystal increased progressively from lignin, through humic acid and coal, to comparatively great size in graphite. His observations suggest that the recementation postulated in the change from low-volatile bituminous coal to anthracite may have resulted from polymerization that increased the carbon content and size of the graphitelike crystal. The possibility of chemical release of carbon at that stage in the metamorphism of coal is suggested by the sharp drop in the hydrogen-carbon ratio from low-volatile bituminous coal through semianthracite to anthracite, as pointed out by White.⁸⁸

⁸⁶ Roberts, J., *Colliery Eng.*, **11**, 170-5 (1934).

⁸⁷ Sedletskii, I. D., and Brunovskii, B., *Kolloid-Z.*, **73**, 90-1 (1935). Sedletskii, I. D., *Trav. inst. Lomonossoff géochim., crist. minéral.*, **8**, 61-70, English abstr. 70 (1936); *Soviet Geol.*, **9**, No. 6, 48-63 (1939); *Khim. Referat. Zhur.*, **1939**, No. 10, 96-7; *Chem. Abs.*, **32**, 1539 (1938), **34**, 6792 (1940).

⁸⁸ White, D., *U. S. Geol. Survey, Bull.*, **382** (1909), 72 pp.

From some point in the subbituminous stage onward to anthracite and graphite, coal may be considered a solid with some included water and gases. Changes in solid coal occur in response to the two main agencies of heat and pressure and consist for the most part of the removal of molecules of water, carbon dioxide, and methane from the various compounds present in the coal. Presumably, the elevated temperatures and pressures to which coals are subjected generally persist over long periods of time. When low-rank coals are heated in the laboratory under pressure in the presence of inert media, progressive changes can be produced that appear to duplicate the changes through the ranks of subbituminous, bituminous, and anthracite. However, the observed temperature at which each rank of coal is produced in such experiments is not necessarily an indication of the temperature required for the formation of that rank of coal by geologic processes. The impossibility of duplicating the pressures that existed in nature and of equaling the long time period of natural coal formation means that such experiments give information on but one of three variables in the process. Studies of coals raised to higher rank by heat from igneous intrusives and computations of the probable temperatures reached yield some information concerning possible temperatures of formation of various ranks of coal. Again, however, the time factor is very small as compared to that available in the broad areas of coal of elevated rank not associated with intrusive masses. It is generally accepted that the speed of reaction doubles with each increase of 10° C in temperature; nevertheless, it is possible that several critical temperatures may exist for the elimination of molecules or radicals from the organic compounds in coal. If this be true,

the combination of long time periods with low temperatures may be ineffective in producing certain of the changes that occur with increase of rank of coal. The only conclusions that can be reached from existing data regarding the temperatures of coal formation are that anthracites are formed at temperatures of not more than 600° C, low-rank bituminous coals at temperatures of not more than 350° C, and subbituminous coals and lignites, in which moisture is important, at temperatures less than 100° C. Coals tend to be coked adjacent to intrusives, but they tend to pass into graphitic coals and graphite in areas of metamorphism not directly related to intrusives. This combination of facts suggests that the graphitization of coal is not a direct function of heat. Pressure must be an important factor in the alteration of coal to graphite, as minor shear planes are common and the high specific gravity of graphite suggests structural reduction of volume. However, the significance of this relationship is more apparent than real, because coal that has been coked near intrusives still retained its coking properties at the time of invasion by hot magmas, whereas the graphitic coals were formed by the action of heat or pressure on anthracites which are noncoking.

The conclusions that can be drawn from our present knowledge concerning the metamorphic agencies that produce the increases in rank of coal have been well summarized by White⁸⁹ in the following statement:

It is hardly to be questioned that the principal advances in the metamorphism (carbonization-devolatilization) of the organic sediments are accomplished at the same times as those of the inorganic rocks—that is, in periods of rock compression and increase of temperature marking orogeny

and diastrophic revolution. At these times, the metamorphic influence of pressure, mainly "horizontal," exerted intermittently and with increasing intensity, always through a long period (time factor), is most effective, with consequent increase of temperature in the rocks, due to heat of compression and friction and to heat of chemical reaction, to which may under some conditions be added heat due to movement of magma of the zone of flow to points nearer the surface of the earth's crust, as beneath anticlinoria.

Finally, it may be stated that the progressive metamorphism of coal through the bituminous and anthracitic ranks is accomplished by a combination of two agencies, increased heat and increased pressure, operating over variable time periods. It seems probable that coal of any one rank can be formed at different temperatures if the pressure and time period are varied, or at different pressures if the temperature and time period are varied, or in different intervals of time if the temperatures and pressures are varied.

Fusain. Fusain (mineral charcoal) is one of the common constituents of coal, but some workers do not believe pure fusain to be coal. In addition, the origin of fusain is quite different from that of the other coal constituents. For these reasons the origin of fusain is considered separately. The mode of origin of fusain has been a source of much speculation. In general, two schools of thought have existed, the first attributing the origin of fusain to charring of plant material in forest fires, and the second to some form of chemical alteration of plant material prior to burial. Karsten⁹⁰ and Rogers⁴ were the earliest proponents of the theory of chemical alteration for the formation of fusain, and Daubrée⁹¹ was the earliest advocate

⁸⁹ Karsten, C. J. B., *Arch. Bergbau Hüttenw.*, **12**, 3-244 (1826).

⁹⁰ White, D., *U. S. Congressional documents*, 73rd Cong., recess, H. Doc. 441, 908 (1934).

⁹¹ Daubrée, A., *Bull. soc. géol. France*, [2] **3**, 153-7 (1846).

of the forest-fire theory. Thiessen¹ in 1913 suggested that dehydration of woody constituents in the peat stage was responsible for the development of fusain. White⁴² believed fusain to be formed by chemical changes occurring in surficial peat-swamp materials during periods of dryness. He believed that under dry conditions some chemical change took place that rendered wood, bast, etc., immune to further subaqueous bacterial decomposition. Stopes and Wheeler¹ attributed the formation of fusain to rapid aerial decay at or near the water surface of the swamp in which most of the debris was submerged. Fox² believed the formation of fusain to be due to carbonization as a result of catalytic action in capillary spaces. Lange and Erasmus⁹² carbonized partly silicified lignites showing well-preserved cell structure by heating under water at 340° C for two hours, then leached out the silica. The residue had been carbonized to fusain with the exception of cell aggregates originally impregnated with bituminous material, which were changed to vitrain. Lange and Erasmus concluded that cell walls filled with humic acids are converted to vitrain, and wood filled with gases, silica, or similar substances as well as wood that had lost its permeability to humic acids through drying are carbonized to fusain. Berl and Keller⁵² called attention to the high lignin content of fusain in brown coals and were of the opinion that fusain is essentially a carbon residue of lignin. Hsiao⁹³ impregnated wood with ammonium or sulfo or phospho compounds and formed charcoal by heating at low temperatures. Hsiao suggested that fossil charcoal was formed by that process and

because of its chemical inertness did not undergo the chemical changes that affected the nonimpregnated debris.

In a special publication edited by Stutzer,²⁸ a dozen students of coal presented their concepts of the formation of fusain. The forest-fire theory was upheld by H. Bode, W. Gothan, E. C. Jeffrey, R. Potonié, and W. Petrascheck. A general theory of desiccation in air was adhered to by A. Duparque, Th. Lange, and D. White. A theory of dehydration by sulfuric acid was advanced by O. Stutzer and K. A. Jurasky. The opinion that fusain has been formed by more than one method was expressed by E. Stach and K. Pietsch.

The general objections to the forest-fire theory that were expressed are: (1) lack of ash layers and ash mixed with fusain such as result from modern fires; (2) improbability of extensive fires in a typical peat swamp; (3) the fact that very fragile plant structures, such as finely veined fern pinnules, are fusainized; (4) the existence of plant stems, such as *Cordaite*s, in which the pithy core is fusainized and the outer part converted to vitrain; (5) the fact that the temperatures required to produce fusain in forest fires would have been so great that resins would have disappeared and also spores, waxes, and other hydrogenous substances would have been fused or destroyed; and (6) the transition from vitrain to fusain in individual wood fragments.

The principal arguments advanced in favor of the forest-fire origin of fusain are: (1) that there is at least apparent similarity between fusain and charcoal formed by fire; and (2) that fragments of charcoal occur in concretions, coal balls, etc., and must have existed as charcoal prior to deposition.

⁹² Lange, Th., and Erasmus, P., *Braunkohle*, **29**, 463-9 (1930).

⁹³ Hsiao, C. C., *Bull. Geol. Soc. China*, **18**, 191-6 (1938).

Lieske⁹⁴ suggested in 1929 that fusain was formed as a result of "gas pockets" developing in the original peat. The plant material in the gas pockets was protected from impregnation with humic derivatives of plant decay and from aerobic decay by a cover of colloidal gels. The resultant anaerobic decay within the gas pocket formed fusain. Hoffmann⁹⁵ pointed out that, though the process described by Lieske might apply to fusain embedded in vitrain, it would not apply to fusain embedded in durain, which must have been porous in the peat stage and shows no evidence of the presence of humic gels to serve as the protective coating. Bergström⁹⁶ has mentioned the formation of coke from resinous gums in sawdust piles where charcoal is formed after spontaneous combustion occurs. It was suggested that spontaneous combustion in piles of forest litter caused peat fires that formed fusain, but the absence of coke in natural fusainized materials is not accounted for adequately.

Thiessen,¹ in discussion after the presentation of his paper "What is Coal," stated that his opinion regarding the origin of fusain was that: ". . . a certain kind of bacteria brought about locally a high temperature, high enough to blacken certain constituents, or bring about a higher state of coalification than the rest of the coal. Similar processes are going on in the peat bogs today. The bacteria are called thermophiles or thermophilic bacteria."

From the data and arguments supplied by the various authors the writer believes most fusain to have been formed by dehydration of plant debris before burial and further loss of volatile constituents

after burial. The general absence of fusain as such in peat together with its general presence in normal banded coal seems to preclude a forest-fire origin for most fusain.

CANNEL AND BOGHEAD COALS

The nature and origin of cannel coal were described by Dawson¹⁷ in 1871, and his ideas have been little modified by later workers. Typical cannel coals are those that are made up chiefly of spores and spore exines. It is generally agreed by workers who have studied cannel coals that they were formed from accumulations of spores, spore exines, and pollens in areas of open water. These materials are believed to have been transported either by water or wind to the site of deposition. The generally high mineral-matter content of cannel coal, the occurrence of most cannel coals in lenticular, channel-shaped bodies, the presence of invertebrate fossils and even fishes in some cannels, and the spore content of the cannels all suggest transportation of the parent material.

After deposition of the spore-rich material the formation of cannel coal apparently is parallel to and a result of the same agencies that form and modify the normal banded coals.

Among studies of boghead or algal coals the work of Bertrand and Renault^{97, 97} has been outstanding. Their numerous publications over a period of about twenty years established most of the modern concepts of composition and origin of the boghead and cannel coals and oil shales.⁹⁸

⁹⁷ Bertrand, C. E., and Renault, B., *Bull. soc. hist. nat. Autun*, **5**, 159-253 (1892). Bertrand, C. E., "Les charbons humiques et les charbons de purins," *Trav. mém. Univ. Lille*, **6**, mém. 21 (1898), 214 pp.

⁹⁸ Zalesky, M. D., *Bull. comité. géol. St. Petersburg*, **33**, 495-507 (1914); *Ann. soc. paléont. Russie*, **1**, 25-42 (1916). Thiessen, R., *U. S. Geol. Survey, Professional Paper* **132**, 126-135

⁹⁴ Lieske, R., *Brennstoff-Chem.*, **10**, 422-4 (1929).

⁹⁵ Hoffmann, E., *ibid.*, **10**, 419-22 (1929).

⁹⁶ Bergström, H., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 794-5 (1931).

Later work on such deposits has confirmed the fundamental concepts of Bertrand and Renault. The first stage of their work substantiated the suggestion of David⁹⁹ that the "yellow bodies" common in oil shales are algal remains. They showed that boghead coals were characterized by abundant algae and cannel coals by abundant spores. Renault particularly showed that the entire group of deposits was formed in open-water areas in which the presence or absence of flocculent humic matter called the "fundamental jelly" determined whether coal or organic shale was formed. In open-water areas associated with peat swamps or other areas of abundant decaying humic debris, the toxic fundamental jelly was present near the bottom and served as a matrix into which the spores of cannel deposits and the algae of boghead deposits settled and were preserved. In the more open-water areas of larger lakes and seas humic decomposition products were present in small amounts only. Spores and algae were more deeply decayed and commonly were mixed with a higher proportion of both clastic and chemically precipitated inorganic matter, and oil shales and canneloid shales were formed. Partly by inference from studies of bogheads and oil shales and partly by direct study, it also was concluded that the fundamental jelly of humic decomposition products was essential to the termination of bacterial decay in the peats that constitute the initial stage of formation of normal banded coals and in addition served as an impregnating material in those coals after the completion of the peat stage.

(1925). Bradley, W. H., *ibid.*, 168, 37-8 (1931). Blackburn, K. B., and Temperley, B. N., *Trans. Roy. Soc. Edinburgh*, 58, 855-69 (1935-6). Skilling, W. J., *Oil Shale and Cannel Coal*, Inst. of Petroleum, London, 1938, pp. 32-8.

⁹⁹ David, T. W. E., *Proc. Linnæan Soc. N. S. Wales*, [2] 4, 483-500 (1889).

NATURE AND ORIGIN OF MINERAL MATTER IN COAL

All coals contain more or less mineral matter, and the problem of its origin is a part of the problem of the origin of coal. The nature and distribution of mineral matter in coal give some information bearing on the conditions of deposition of the coal-forming materials, and it is possible that some inorganic constituents of the mineral matter have entered into reactions with organic compounds and thus played a direct part in the transformation of plant material into coal.

Lessing¹⁰⁰ classified the mineral constituents of coal as follows: (1) the residue of the mineral constituents of the plants from which the coal is derived; (2) detrital matter, blown, washed, or settled into the deposit; (3) saline deposits from water with which the plants or plant residues were in contact before and during coal formation; (4) crystalline deposits from waters which percolated the coal seams through cracks and fissures during and after coal formation; (5) products of decomposition of the above substances and of interaction between themselves and the coal substances. He also pointed out that part of the inherent ash of the original plants or of the minerals from other sources may have been removed during or after the process of coal formation. He analyzed the ashes from the four main constituents of Hamstead "thick coal" and obtained the results given in Table II.

Lessing considered the ash of clarain and vitrain largely inherent plant ash, that of durain largely detrital clay particles, and that of fusain together with that found in cleats and partings largely material deposited from infiltrating solu-

¹⁰⁰ Lessing, R., *J. Soc. Chem. Ind.*, 44, 277-83 (1925).

TABLE II

COMPOSITION OF THE ASHES FROM THE FOUR
MAIN CONSTITUENTS OF HAMSTEAD "THICK
COAL" REPORTED BY LESSING¹⁰⁰

	Fusain percent	Durain percent	Clarain percent	Vitrain percent
SiO ₂	8.84	50.54	9.44	6.08
Al ₂ O ₃	8.66	42.34	16.58	15.49
Fe ₂ O ₃	3.37	1.36	3.31	3.09
MnO	0.51	0	0.23	0.13
TiO ₂	0.04	0.44	0.50	0.24
CaO	57.00	3.69	12.98	15.22
MgO	1.30	0	10.52	1.87
Na ₂ O	3.24	0	15.71	17.67
K ₂ O	0.67	0	0.20
SO ₃	14.65	3.23	32.18	30.89
P ₂ O ₅	0.01	trace
CO ₂	2.98	6.69
	101.26	101.60	101.46	97.57
Soluble in H ₂ O	16.57	3.48	65.24	69.52
Soluble in HCl	71.38	23.81	17.86	20.46
Insoluble in HCl	12.05	72.71	16.90	10.02
	100.00	100.00	100.00	100.00

tions. In Lessing's opinion the data supplied by his studies, so far as they bear on the origin of coal, indicated that clarain and vitrain consist of pure plant remains, whereas durain contains much clay mixed with small plant entities. Lessing believed this to indicate that durain was formed in deeper water than vitrain and clarain and was subjected to contamination by transported mineral debris.

Ball¹⁰¹ has made a thorough study of the mineral matter contained in a complete section of a coal bed. He found both detrital material that had been introduced at the time of peat formation, and secondary minerals that had formed after the deposition of the coal-forming material. The common detrital material was clay, but present also in small amounts were quartz, feldspar, garnet, common hornblende, apatite, zircon, muscovite, epidote, biotite, augite, kyanite, rutile, staurolite,

topaz, tourmaline, and chloritic material. The secondary minerals were: (1) kaolinite, which occurred as fillings of vertical desiccation cracks in vitrain and cleat joints and as impregnations of fusain; (2) calcite, as the principal mineral fillings of the longer cleat joints; and (3) pyrite (marcasite) as layers, nodules, fillings of cracks and joints, impregnations, and scattered aggregates.

Lessing¹⁰² considered the distribution of coal ash in vitrain, fusain, and durain. Fusain ash was highly variable, consisting mostly of calcium carbonate and iron carbonate, and apparently was deposited from percolating waters. Durain ash consisted largely of aluminum silicates (clay minerals) and was a function of the attrital nature of durain. Vitrain (and clarain) ash represented the original plant ash or its residue.

Hickling¹⁰³ found the mineral matter to be much the same as that given by Ball, and the distribution to be similar to that given by Lessing. Attention was called to the low ash content of vitrain, which was generally less than 1 percent. The vitrain ash was less than that of the original plant materials and also higher in iron content than initial wood ash, which indicates that the residual plant ash is not the same as the original plant ash. Haas¹⁰⁴ has tabulated the elements present in plants which are to be expected in coals. The elements sulfur, phosphorus, potassium, calcium, magnesium, and iron are essential to the existence of all plants. Silicon, chlorine, sodium, manganese, iodine, and aluminum are found in the ashes of certain plants and may be essential for those plants. The ash content of land plants ranges from

¹⁰² Lessing, R., *Proc. 1st Intern. Conf. Bituminous Coal*, 1926, 165-85.

¹⁰³ Hickling, H. G. A., *Trans. S. Wales Inst. Engrs.*, 46, 932-6 (1931).

¹⁰⁴ Haas, P., *Fuel*, 4, 424-9 (1925).

¹⁰¹ Ball, C. G., *Illinois State Geol. Survey, Rept. Investigations* 33 (1935), 106 pp.

less than 1 percent in wood to an average of 8 to 12 percent in leaves. Aquatic plants are generally higher in ash than land plants, algae averaging from 10 to 40 percent, though some contain as much as 60 percent. Zalessky¹⁰⁵ showed that some coals have less ash than is found in the plant families represented in the coal. This observation, which recurs particularly in discussions of vitrain, suggests that some mineral matter is extracted from the original plant material during the process of coalification. It is confirmed to a certain degree by the recognition in peat and lignite of calcium ulmates, or humates, by Websky¹⁰⁶ and of whewellite (calcium oxalate), humboldtine (ferrous oxalate), and mellite (an aluminum salt of mellitic acid) by Clark.¹⁰⁷ Other investigators, such as van Bemmelen¹⁰⁸ and Baumann and Gully,¹⁰⁹ have contended that humins in the form of hydrosols or hydrogels will absorb inorganic salts which cause their precipitation. Odén¹¹⁰ has shown that humins are acids with replaceable hydrogen which permits the formation of salts with alkalies. Fuchs⁴⁴ has found abundant humates in brown coal, calcium humate being insoluble. It appears probable from these data that some of the inorganic material in the original plants may react with organic derivatives to form soluble compounds which are lost, thus reducing the content of inorganic material. Fischer and Bahr¹¹¹ demonstrated base-exchange

reactions in humates that may produce either soluble or insoluble materials and consequently may play an important part in the early stages of coal formation.

Briggs¹¹² and Goldschmidt and Peters¹¹³ recorded the presence in coal ash of vanadium, titanium, manganese, barium, gold, silver, copper, lead, zinc, tin, arsenic, antimony, uranium, germanium, beryllium, boron, scandium, yttrium, platinum, cobalt, and cadmium. Goldschmidt and Peters found the rare elements to be more common in low-ash coals and concluded that they occur in plant ash rather than in ash from extraneous material. Lessing¹¹⁴ reported fluorine, probably from fluorite as an extraneous impurity, present in one coal in sufficient quantity to cause disintegration of porcelain tower fillings in gas works.

Experiments on anthracites conducted by Turner¹¹⁵ showed a concentration of ash in the duller bands and even distribution in the brighter laminae, and suggested that the inorganic constituents are not combined chemically with the organic matter to any marked extent. However, such conclusions do not preclude the possibility of chemical combination of organic and some inorganic matter in the earlier stages of coal formation.

Detrital clay minerals, with their exchangeable bases, may play an important part in the early stages of coal formation, as may also calcium carbonate and pyrite. However, data are too few to show what effect they and the rarer inorganic constituents of coal may have had in the process of coal formation.

¹⁰⁵ Zalessky, M. D., "Histoire naturelle d'un charbon," *Mém. comit. géol. Petrograd*, **139**, new ser. (1915), 74 pp.

¹⁰⁶ Websky, A., *J. prakt. Chem.*, **92**, 86 (1864).

¹⁰⁷ Clark, F. W., *U. S. Geol. Survey, Bull.* **770**, 759 (1924).

¹⁰⁸ Van Bemmelen, J. M., *Die Absorption*, Theodor Steinkopff, Dresden, 1910, 548 pp.

¹⁰⁹ Baumann, A., and Gully, E., *Mitt. bayr. Moorkulturanstalt*, **4**, 31-156 (1910).

¹¹⁰ Odén, S., *Ber.*, **45**, 651-60 (1912).

¹¹¹ Fischer, F., and Bahr, T., *Brennstoff-Chem.*, **15**, 245-50 (1934).

¹¹² Briggs, H., *Fuel*, **13**, 303-4 (1934).

¹¹³ Goldschmidt, V. M., and Peters, C., *Brennstoff-Chem.*, **14**, 410 (1933). Goldschmidt, V. M., *Ind. Eng. Chem.*, **27**, 1100-2 (1935).

¹¹⁴ Lessing, R., *Fuel*, **13**, 347-8 (1934).

¹¹⁵ Turner, H. G., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 627-41 (1930).

CHAPTER 2

CLASSIFICATION OF COAL

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Coal is one of the world's leading commodities, whether measured in terms of tonnage produced, monetary value, or industrial importance. Because of the widespread occurrence of coal deposits, the numerous varieties which are available, and the diversity of uses, a great many methods of coal classification have been used during the past 100 years. These classifications have been designed to serve many special interests, ranging from the scientific viewpoints of geologists, paleobotanists, and research chemists, to the practical viewpoints of transportation agencies, coal salesmen, and combustion engineers.

Many of the classifications require a knowledge of the chemical composition or physical properties of coal, or even a detailed microscopic investigation, whereas other methods of classification are based on such simple and obvious factors as the geographic location of coal deposits, the railroads which serve the mines, or the size of lumps. The most voluminous classification in use today relates to prices that may be charged for bituminous coal and is based chiefly on prior marketing practices and average production costs.

Practically every chemical and physical characteristic of coal, as well as every item of its commercial description, has been used or seriously proposed for classification purposes. The literature on coal clas-

sification is so voluminous, and overlaps so extensively with the other subjects in this volume, that a considerable degree of selection has been necessary in preparing this chapter. Nevertheless some duplication of material has been unavoidable.

Emphasis has been placed on recent methods of classification which have received widest acceptance, or which seem to be of greatest interest and value to scientific and technical readers. References to various foreign classifications are included, but attention has been directed principally to the coals of the United States and Canada, which comprise about two-thirds of the world's known reserves and include a rather complete range of types, ranks, and grades of coal.

CLASSIFICATION BY TYPE

Because of the way in which coal deposits have been formed, they are highly variable. The "type" depends upon the nature and biochemical alteration of the original plant ingredients; the "rank," upon their subsequent alteration by dynamochemical processes in the series peat to anthracite; and the "grade," upon the amount and nature of the mineral impurities associated with the coal.

Coal Is a Rock, Not a Mineral. "Coal is a rock, since the geologist regards as rocks all natural, solid substances, organic

or inorganic, that compose the earth's crust. In trade, industry, and legal affairs it is also considered a mineral, and it is sometimes spoken of as *mineral coal*. In a restricted technical sense, however, it is not a mineral, as such a substance is defined by Dana, our standard authority on minerals. A mineral, according to Dana, is an inorganic, homogeneous substance with a definite chemical composition, all of which requirements coal lacks."¹

It has long been known that coal is derived from plants; in fact, coal contains a large proportion of material which retains much of the original plant structure in a good state of preservation. In 1833, Hutton² described plant cells found by the microscopic examination of coal and concluded that "every variety of coal is of vegetable origin" and that "the difference of the nature of these varieties has most probably arisen from an original difference in the nature of the vegetables of which they are composed."

A summary of coal paleobotany by Thiessen and Sprunk³ points out that three classes of plants are easily recognized in coal, namely: coniferouslike, cycadophyte or fernlike, and lycopods (which were trees related to present club mosses). These are not mixed promiscuously throughout the coal but are separately aggregated, and usually one class of plants predominates in a given coal bed or layer.

GEOLOGIC CLASSIFICATION

The geologic age of coal deposits is also of interest in this connection, because of the great change in the character and pre-

dominant types of vegetation during the period of perhaps 200,000,000 years during which coal deposits have been forming. Whereas deposits of vegetal matter occur even in pre-Cambrian rocks, land plants did not become sufficiently abundant to form coal deposits until the Upper Devonian, and little coal of present commercial character was laid down until the Carboniferous Age.

Geologic age is one of the oldest methods of classifying coal, and it is always stated in a comprehensive discussion of coal deposits. Table I summarizes the

TABLE I
GEOLOGICAL FORMATIONS WHICH CONTAIN
COAL

Era	System, Age, or Period	Series or Epoch
Cenozoic	Quaternary	Recent Pleistocene
	Tertiary	Pliocene Miocene Oligocene Eocene
Mesozoic	Cretaceous Jurassic Triassic	Cretaceous Jurassic Triassic
Paleozoic	Carboniferous	Permian Pennsylvanian Mississippian
	Devonian	Devonian

geological ages in which coal deposits occur.

Thiessen has briefly described the characteristic plant growth during each pe-

¹ Moore, E. S., *Coal—Its Properties, Analysis, Classification, Geology, Extraction, Uses and Distribution*, John Wiley & Sons, New York, 2nd ed., 1940, p. 3.

² Hutton, W., *Phil. Mag.*, 2, 302-4 (1833).

³ Thiessen, R., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 631* (1941), 56 pp.

riod.⁴ Gruner and Bousquet⁵ have summarized the types of flora in the principal coal deposits of the world. For a comparison of the names used for coal-bearing strata in the United States, Great Britain, France, Germany, and Australia, see Moore,⁶ who presents 113 pages on the geologic and geographic distribution of coal throughout the world, with many maps and tables. The same reference includes information on the relative importance of coal deposits of each geologic age and rank, in the various countries.

CLASSIFICATION ACCORDING TO BANDED STRUCTURE

Thiessen, in well-illustrated papers,^{7, 8} has traced the steps by which living plant tissues have been converted into coal of various types and ranks.

For a discussion of coal petrography, see

summary at this point will serve to explain classification according to banded structure and type.

Most coals have a laminated structure consisting of layers which may vary widely in thickness, luster, and texture. This banded structure persists in all ranks of coal from lignite to anthracite but is usually most obvious in bituminous coals. Careful examination of large polished vertical faces of common bituminous coal shows that the jet black, glossy layers of "anthraxylon" or "vitrain" are of limited lateral extent and are embedded in a continuous ground mass of variable "attritus," which is grayer, duller in luster, and tougher. Layers of "fusain" or "mineral charcoal" may also be present, as well as layers or inclusions of mineral impurities.

Table II presents a classification based on banded structure.¹⁰

TABLE II

CLASSIFICATION OF COAL ACCORDING TO BANDED STRUCTURE

Designation	Thickness of Bands millimeters	Remarks
Coarsely banded	>2	
Finely banded or striped	2-0.5	
Microbanded or striated	<0.5	Bands not visible to naked eye
Mixed banded		Both coarse and fine bands
Nonbanded (little or no lamination)		Cannel and boghead coals which break with conchoidal fracture

Chapter 3 of this volume, and also a symposium of six papers on the physical constitution of coal.⁹ However, a brief

Detailed descriptions of the banded components of many coal seams are available. For American coals, the U. S. Bureau of Mines has issued a series of publications on the carbonizing properties and petrographic composition of various coals, which

⁴ Thiessen, R., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 419-35 (1930).

⁵ Gruner, E., and Bousquet, G., *Atlas général des houillères*, Comité Central des Houillères de France, Paris, 1911, Pt. 2, p. 14.

⁶ Moore, E. S., p. 348 of ref. 1.

⁷ Thiessen, R., *Proc. Fuel Engrs. Appalachian Coals, Inc.*, 4, 211-72 (1937), 5, 112-74 (1937).

⁸ Thiessen, R., *Proc. 2nd Intern. Conf. Bituminous Coal*, 1, 695-767 (1928).

⁹ Cady, G. H., *J. Geol.*, 50, 337-56 (1942). Lowry, H. H., *ibid.*, 50, 357-84 (1942). Mar-

shall, C. E., *ibid.*, 50, 358-405 (1942). McCabe, L. C., *ibid.*, 50, 406-10 (1942). Sprunk, G. C., *ibid.*, 50, 411-36 (1942). Dapples, E. C., *ibid.*, 50, 437-50 (1942).

¹⁰ Davis, J. D., Reynolds, D. A., Sprunk, G. C., and Holmes, C. R., *U. S. Bureau Mines, Tech. Paper 630* (1941), 45 pp.

have been indexed.¹¹ For English coals, pamphlets entitled *Physical and Chemical Survey of the National Coal Resources*^{12, 13} are available. Both series of publications make use of shading with lines and dots to indicate the various banded structures in graphic representations of coal-seam profiles.

Excellent photographs showing the banded structure of American bituminous coals will be found in various U. S. Bureau of Mines publications. They illustrate the natural surfaces of vertical cleavage planes¹⁰ or polished surfaces,^{14, 15} and some of these references also show photomicrographs of thin sections of the same coals.

Seyler¹⁶ and Turner^{17, 18} have described the petrology of anthracite. Bode¹⁹ has also pointed out that all coal constituents tend to become bright when transformed into high-rank coal.

TERMINOLOGY FOR COAL COMPONENTS

The original coal-forming plant materials deposited in primeval swamps varied according to the geological period and the

environment. After deposition they underwent a variable biochemical process of semiroting, maceration, and elimination under the influence of micro-organisms. Differences in the resulting unconsolidated peat or equivalent deposits are the basic cause of differences in coal "types." Subsequent alteration of the peat deposits by geologic forces acting through millions of years has led to differences in "rank."

At the present time there is no general agreement as to the best way of defining coal types. Some prefer to define them in terms of the predominant plant components as revealed by microscopic examination; others use lithological terms based on hand specimens of coal considered as a rock, plus physical or chemical tests in some cases. Each method has advantages and limitations, and in comprehensive scientific descriptions of coal deposits all these viewpoints now receive attention.

Several tables which follow show the relation of the banded constituents of coal to various classification problems. These tables contain quantitative data selected from U. S. Bureau of Mines publications, whose nomenclature has therefore been followed. Since many different terms have been used throughout the world to designate the various layers or petrologic constituents of coal, a partial correlation of such terms is presented in Table III for the reader's convenience.

Anthraxylon. The thicker layers of anthraxylon were derived from undisintegrated wood and bark of plants such as stems, branches, and roots, or their fragments, which were flattened and coalified. The thinner bands may reveal almost any organ of a plant, more or less well preserved.³ There may be resinous cell fillings or inclusions. Anthraxylon represents unit plant increments which have been preserved in the coal bed, and it is of

¹¹ Wilson, J. E., and Davis, J. D., *U. S. Bur. Mines, Tech. Paper 637* (1942), 10 pp.

¹² *Dept. Sci. Ind. Research (Brit.), Fuel Research Survey Papers*, 1922 to date. Check list and reports obtainable from H. M. Stationery Office, London, York House, Kingsway, W. C. 2.

¹³ Sinnatt, F. S., *Trans. Inst. Mining Engrs. (London)*, **63**, 307-17 (1922).

¹⁴ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **344** (1931), 107 pp.

¹⁵ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Papers* **519** (1932), 78 pp., **524** (1932), 60 pp., **525** (1932), 60 pp., **531** (1932), 44 pp., **542** (1932), 60 pp., **548** (1933), 52 pp.

¹⁶ Seyler, C. A., *Fuel*, **2**, 217-8 (1923).

¹⁷ Turner, H. G., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 127-48 (1925).

¹⁸ Turner, H. G., *ibid.*, **88**, 627-41 (1930); *Fuel*, **11**, 254-61 (1932).

¹⁹ Bode, H., *Kohle u. Erz*, **29**, 320-1 (1932); *Chimie & industrie*, **29**, 551 (1933).

TABLE III

CORRELATION OF TERMS DESIGNATING PETROLOGIC CONSTITUENTS OR TYPES

<i>U. S. Bureau of Mines Usage</i>	<i>Approximate Equivalents</i>
Anthraxylon	Vitrinite (collinite if devoid of structure, and tellinite if structure can be shown); vitrain, vitrite, Vitrit.
Fusain	Fusinite; fusite, Fusit; mineral charcoal, mother of coal; Faserkohle.
Attritus	Groundmass. Attritus is a broad term referring to macerated plant debris from any source, intimately admixed with mineral matter and coalified. It predominates in splint, cannel, and boghead coals, and may be present in large amount in bright coals. The U. S. Bureau of Mines terminology recognizes two distinct types of attritus, which are designated by the appearance of thin sections by transmitted light (for coals of bituminous or lower rank):
Translucent attritus	Vitrinite plus exinite plus resinite.
Opaque attritus	Micrinite plus semifusinite plus fusinite.
Bright coal	Clarain plus vitrain; clarite plus vitrite; Clarit plus Vitrit; humic, woody, or xyloid coal; common coal; Glanzkohle.
Splint coal	Durain, durite, Durit; micrinite plus exinite; hards or dulls; Mattkohle or Streifenkohle.

lower ash content than the attritus with which it is associated.

Since the thicker layers of anthraxylon (vitrain) represent a fairly uniform plant constituent which can often be isolated in quantities sufficient for test purposes, anthraxylon is frequently used for classification purposes as the standard component with which to compare the more variable attrital layers of the same coal.

Fusain. Fusain resembles charcoal; it may be formed from cells or tissues of any kind but is commonly derived from wood.

All intermediate stages between normal coal and typical fusain are found. The cause of this state of coalification is uncertain and much debated.^{20, 21} Fusain is noncoking and has less volatile matter than the remainder of the coal. It occurs to the extent of zero to 10 percent by weight, being most evident in bituminous coals, in which it is typically soft and friable, forming planes of weakness along which the lumps of coal tend to split horizontally. Fusain is the black smut in "soft coal." Being porous, it is subject to mineralization by infiltrating ground waters, so that its hardness and ash content are quite variable.

Fusain is one component which may be determined by analytical methods other than microscopic estimation.^{21, 22, 23}

Attritus. Attritus is coalified plant debris consisting of the more resistant plant matter remaining after the original debris has undergone maceration, weathering, and alteration by micro-organisms. Thiessen and Sprunk stated that the following constituents may be recognized:^{20, 24} (1) translucent cell-wall degradation matter or translucent humic matter; (2) brown cell-wall degradation matter or brown matter; (3) granular opaque matter; (4) more highly carbonized matter, fusain; (5) resins, tannins; (6) waxes; (7) spore exines, pollen exines, cuticles; (8) mineral matter; and (9) algal remains, especially in boghead coals.

²⁰ Thiessen, R., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 504* (1935), 71 pp.

²¹ Davis, J. D., *U. S. Bur. Mines, Information Circ. 6115* (1929), 10 pp.

²² Fuchs, W., Gauger, A. W., Hsiao, C. C., and Wright, C. C., *Penna. State Coll., Mineral Ind. Exp. Sta., Bull. 23* (1938), 43 pp. Parks, B. C., Land, G. W., and Rees, O. W., *Ind. Eng. Chem., Anal. Ed.*, **14**, 303-5 (1942).

²³ Fieldner, A. C., and Schmidt, L. D., *U. S. Bur. Mines, Circ. 7190*, 12 (1941).

²⁴ Thiessen, R., *U. S. Geol. Survey, Professional Paper 132-I*, 121 (1925).

Attritus is therefore a very broad term which includes components that are quite different in their chemical and physical nature. In fact, three of the four principal types of coal are always predominantly attrital, and many specimens of the fourth type are attrital. Therefore, qualifying adjectives are necessary to differentiate between varieties of attritus. Thiessen and

examined in thin sections by transmitted light by means of a microscope.

They used the term "translucent attritus" to indicate item 1 in the above list, that is, translucent cell-wall degradation matter, which may be thought of as fragmented anthraxylon, and also for the quite different items 5, 6, 7, and 9, but with a further qualification as to whether the attritus is

TABLE IV
COMMONLY RECOGNIZED TYPES OF COALS CHARACTERIZED
ACCORDING TO THEIR ANTHRAXYLON AND ATTRITUS ²⁵

Type Name of Coal	Relative Amounts of Anthraxylon and Attritus	Nature of Attritus	Structure of Coal
<i>Banded coals</i>			
Common or bright	Either anthraxylon or attritus may predominate	Translucent humic matter pre- dominates unless coal is too far altered in rank. Spores, resins, fusain fragments, cuticles, and minor amounts of opaque mat- ter present.	Coarsely, finely, or microbanded. Bright luster
Splint	Attritus predom- inating	Opaque matter predominating in coals or layers of ranks in which the attritus is generally trans- lucent. Salver-shaped spore exines usually abundant. Other spores and translucent humic matter, resins, and fusains present.	Finely or micro- banded. Com- pact. Hard. Irreg- ular fracture. Dull luster.
<i>Nonbanded coals</i>			
Cannel	Mostly attritus	Humic matter may be translucent or opaque. Spore or pollen exines frequently predominate. Algae may be present in minor amounts.	Compact, conchoidal fracture.
Boghead	Mostly attritus	Algae abundant. Spores may be present in minor amounts.	Compact, conchoidal fracture.

Sprunk used terms based on the color and appearance of bituminous coal layers when

rich in resins, waxes, spores and pollen exines, cuticles, or algae.

"Opaque attritus" includes item 2, the brown cell-wall degradation matter which characterizes splint coals, and item 3, which is prominent in semisplints. "New evi-

²⁵ Adapted from *Am. Soc. Testing Materials, Sectional Comm. on Classification Coal, Gen. Circ. 41, Sub. Comm. II, Rept. 6, 1933.* Fieldner, A. C., et al., p. 25 of ref. 14.

dence . . . confirms the belief that the splint coals were laid down under conditions especially favorable to the action of biological agencies, thus bringing about a high degree of decomposition and maceration of the plant material. The opaque matter results from such an advanced state of decomposition; and the further the decay progressed, the more opaque matter was formed and the greater its degree of opacity."²³

Table IV describes the four commonly recognized types of coal according to their components, using the U. S. Bureau of

Mines terminology which has just been described.

A semisplint type has also been described,¹⁴ in which anthraxylon and attritus are present in more or less equal proportions and granular opaque matter is very prominent. In general, it corresponds with coal known to the trade as "block coal."

After the foregoing brief summary of nomenclature, the reader will be prepared to examine some of the data regarding American coal seams which have been reported by the U. S. Bureau of Mines.

TABLE V

RANGE OF PERCENTAGES OF COAL TYPES AND COMPONENTS IN THIRTY-NINE SEAMS OF U. S. BITUMINOUS COAL EXAMINED FOR GAS-, COKE-, AND BYPRODUCT-MAKING PROPERTIES, ALSO SPLINT COALS

Seam	State	Types				Components				Ref.
		Bright	Semi-splint	Splint	Can-nel	Anthrax-ylon	Trans-lucent Attritus	Opaque Attritus	Fusain	
No. 6	Illinois	100	70	24	1	5	26
Lower Kittanning	Pennsylvania	100	68	24	7	1	27
Upper Kittanning	Pennsylvania	100	66	18	13	3	27
Black Creek	Alabama	100	45	38	7	10	28
Lower Sunnyside	Utah	100	30	61	6	3	29
No. 2 Gas	West Virginia	50	45	5	41	44	12	3	30
Lower Banner	Virginia	36	53	11	30	49	19	2	31
Dorothy	West Virginia	17	20	63	17	48	33	2	32
Coalburg	West Virginia	32	68	33
Brookville	Pennsylvania	5	88	7	33

²⁶ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 524* (1932), 60 pp.

²⁷ Fieldner, A. C., Davis, J. D., Thiessen, R., Selvig, W. A., Reynolds, D. A., and Holmes, C. R., *ibid.* **595** (1939), 83 pp.

²⁸ Fieldner, A. C., Davis, J. D., Thiessen, R., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *ibid.* **531** (1932), 44 pp.

²⁹ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph 5* (1934), 164 pp.

³⁰ Fieldner, A. C., Davis, J. D., Thiessen, R.,

Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 548* (1933), 52 pp.

³¹ Fieldner, A. C., Davis, J. D., Reynolds, D. A., Brewer, R. E., Sprunk, G. C., and Schmidt, L. D., *ibid.* **616** (1941), 47 pp.

³² Fieldner, A. C., Davis, J. D., Selvig, W. A., Thiessen, R., Reynolds, D. A., Holmes, C. R., and Sprunk, G. C., *U. S. Bur. Mines, Bull.* **411** (1938), 162 pp.

³³ Sprunk, G. C., Ode, W. H., Selvig, W. A., and O'Donnell, H. J., *U. S. Bur. Mines, Tech. Paper 615* (1940).

Table V presents the maximum and minimum percentages of coal types and components which were found in the examination of pillar samples from thirty-nine seams of bituminous coal which were tested for gas-, coke-, and byproduct-making properties. The last two samples are from a separate investigation relating to splint coals.

Table V does not include any cannel or

CORRELATION OF COAL TYPES WITH CHEMICAL PROPERTIES

The chemical analysis and physical properties of the various coal types are profoundly affected by the "rank" of coal, that is, its degree of coalification, which is discussed later in this chapter. White³⁷ has presented diagrams to show the change in carbon, hydrogen, and oxygen contents of humic, cannel, and boghead coals as they

TABLE VI
ADDITIONAL COALS HAVING HIGH OR LOW PERCENTAGES
OF PETROGRAPHIC COMPONENTS

Description	County or Seam	State	Components			
			Anthrax- ylon	Translucent Attritus	Opaque Attritus	Fusain
Cannel	Sevier County	Utah	4	92 *	4	0
Cannel	Floyd County	Kentucky	0	51 †	49	0
Subbituminous B	Monarch Seam	Wyoming	76	20	3	1

* Woody degradation matter predominates.

† Spores predominate.

boghead coals, but the percentages of petrographic components for nine such coals from Kentucky, Ohio, Utah, West Virginia, and Virginia have been published.³⁴ Percentages of components in various western United States lignites and subbituminous coals are also available.^{35, 36} These extend the maximum and minimum percentages of petrographic components, as shown in Table VI.

³⁴ Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., Fein, M. L., and Storch, H. H., *Fuel*, **19**, 84-9 (1940).

³⁵ Fisher, C. H., Sprunk, G. C., Eisner, A., Fein, M. L., and Storch, H. H., *ibid.*, **19**, 186-95 (1940).

³⁶ Fieldner, A. C., and Schmidt, L. D., p. 54 of ref. 23.

are transformed from peat through lignite, subbituminous, and bituminous coal stages to anthracite and graphite. He considered that chemical differentiation persists into the "semibituminous" (low-volatile bituminous) rank.

For the present purpose of comparing types and components, differences due to rank will be avoided as far as possible. The simplest assumption is that all the banded constituents in a pillar sample of coal have been subjected to the same geologic influences following the peat stage, and therefore are of the same rank, geo-

³⁷ White, D., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 253-81 (1925).

logically speaking. Since the coal types and components in a given sample may vary considerably, they may not all have the same "rank" when compared by chemical and physical criteria.

Variations in the petrographic and chemical composition of the layers of a single seam of coal are illustrated in Tables VII, VIII, and IX, based on face samples cut from a mine operating in the Chilton

sents the petrographic composition inch by inch and shows that the above layers vary widely within themselves. Thiessen⁷ has shown that the petrographic constituents of this seam vary much more in chemical analysis than the generalized layers of Table VII. For example, Table VIII shows that pure anthraxylon yielded 34.2 percent volatile matter and the fusain only 19.8 percent. The pure opaque attritus

TABLE VII
ANALYSIS OF LAYER SAMPLES OF CHILTON SEAM³⁸

Layers	Thickness of Layers	Petrographic Composition				Proximate Analysis, Dry Basis	
		Anthrax- ylon	Attritus		Fusain	Volatile Matter	Ash
			Trans- lucent	Opaque			
	inches	percent	percent	percent	percent	percent	percent
1. Bright coal	4.9	41	52	3	4
2. Semisplint, com- paratively few spores	7.9	21	56	18	5	35.3	6.5
3. Bright coal	25.2	40	50	8	2	37.5	3.0
4. Semisplint, rich in spores	9.0	23	54	20	3	38.7	3.7
5. Bright coal	5.4	47	44	8	1
6. Gray splint	10.8	14	43	41	2	31.9	9.7
Total seam	63.2	32	49	16	2.7	36.8	5.3

seam, Logan County, West Virginia. This coal seam was divided, on the basis of appearance, into six principal layers, as shown in Table VII.

The original reference graphically pre-

yielded 24.7 percent volatile matter, while the spore-rich attritus gave 42.1 percent. The entire seam has been classified into types and subtypes of coal,¹⁴ as shown in Table IX.

Proximate and ultimate analyses, calorific values, softening temperatures of ash, agglutinating values of mixtures with sand, and yields of coke and byproducts are also

³⁸ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 542* (1932), 60 pp.

TABLE VIII

ANALYSIS OF PETROGRAPHIC CONSTITUENTS OF
CHILTON SEAM ⁷

Sample	Dry, Ash-Free Basis		As Received Basis
	Volatile Matter	Hydrogen	Ash
	percent	percent	percent
Pure anthraxylon	34.2	5.4	2.2
Pure opaque attritus	24.7	4.5	9.1
Spore-rich attritus	42.1	5.9	2.8
Fusain	19.8	4.0	8.6
Total pillar section	39.4	5.7	4.4

TABLE IX

TYPE AND SUBTYPE COALS IN THE CHILTON
SEAM ³⁸

Type	Percent
Bright coal	56
Semisplint	27
Splint	17
<i>Subtype</i>	
Attrital coal (more than 75 percent attritus)	44
Attrital-anthraxylous (50 to 75 percent attritus)	56
Anthraxylous-attrital (50 to 75 percent anthraxylon)	0
Anthraxylous (more than 75 percent anthraxylon)	0

available for the total coal and for layers 2, 3, 4, and 6 shown in Table VII.

The great effect of resins and spores on the chemical analysis of coals is indicated by Table X.

If a splint coal has few or no spores, it usually will have 3 to 15 percent less volatile matter than the accompanying bright coal, but the presence of a substantial proportion of spores tends to offset or reverse this low volatile-matter yield of the typical splint-forming constituents.

TABLE X

CHEMICAL ANALYSIS OF RESINS AND SPORES
ISOLATED FROM COAL ³³

	Analysis on Dry Basis			
	Volatile Matter	Hydrogen	Ash	Btu per Pound
	percent	percent	percent	
Resins from coal at Merritt, British Columbia	94.3	10.1	1.8	16,950
Spores from coal at Williamston, Mich.	68.9	6.9	10.0	13,820

A comparison has been made of the chemical analyses and low-temperature carbonization products of bright and splint coal from each of seventeen seams of bituminous coal obtained in West Virginia, Kentucky, Virginia, and Alabama.³³ It was concluded that:

In all instances the splint coals have a higher carbon content than the bright coals of the same beds, and generally they have a higher ash content, higher ash-fusion temperature, and higher calorific value. On the other hand, the bright coals generally have the highest moisture, hydrogen, nitrogen, and oxygen values.

The yield of low-temperature carbonization products was determined by the Fischer assay method:

On the dry, mineral-matter-free coal basis, each of the splint coals gave a smaller yield of water of decomposition and in every instance but one a smaller yield of gas than does its associated bright coal. The yield of coke and of tar and oil of splint coal may be higher or lower than bright coal depending on the analyses of the coals. Likewise the calorific value of the gas may vary in either direction, but the Btu of the gas per pound of coal carbonized is nearly always less for the splint coals. Except for the coals of higher oxygen content, the coke

residue from the bright coals is considerably more swollen and cellular than from the splint coals. . . . With the exception of the Millers Creek coal, the agglutinating value of the splint coals tested is always less than that of the associated bright coal.

The same reference presents graphic studies of the suggestions of Fisher³⁹ and Seyler⁴⁰ that there is a relationship between the petrographic composition, volatile matter, and carbon-to-hydrogen ratio of coals. It was concluded that:

. . . in most cases either Seyler's volatile displacement or Fisher's hydrogen-carbon ratio can be used to distinguish between bright and splint coals; but, inasmuch as so many of the coal beds are mixtures, it probably would be very difficult to identify, by either method, the type of coal from ultimate and proximate analyses of face or seam samples.

Seyler's paper should be studied by anyone who is interested in this subject.

The references already cited show that it is possible to describe coals systematically in terms of their structure. However, the *quantitative* classification of coals into types, subtypes, and petrographic constituents by macroscopic and microscopic examination of face samples requires very specialized knowledge and technique. After the mass of information needed for such classification has been obtained, it is still necessary, for practical purposes, to determine various chemical and physical properties of the coals.

Coal petrography has been of invaluable service in providing a scientific explanation of differences which may exist in coals of similar average chemical composition. However, it has not yet been

found practical to base a commercial system of coal classification on coal structure as revealed by the microscope. A satisfactory quantitative method is needed for use on commercial shipments, as distinct from the examination of column samples cut from the coal seam.

Beginning in 1932, an American Society for Testing Materials subcommittee consisting of coal geologists and chemists attempted to develop a set of recommendations for the type classification of coal. After four years of meetings and correspondence, the subcommittee reported⁴¹ that the present state of knowledge did not permit the preparation of A.S.T.M. specifications or definitions covering types of coal based on origin.

Since it was desirable for commercial purposes to have definitions of coal varieties other than those of rank and grade, another committee prepared the following definitions,⁴² which were adopted as standard in 1939.

STANDARD DEFINITIONS FOR COMMERCIAL VARIETIES OF BITUMINOUS AND SUBBITUMINOUS COALS

A.S.T.M. Designation: D493-39

Common Banded Coal. The common variety of bituminous and subbituminous coal. It consists of a sequence of irregularly alternating layers or lenses of (1) homogeneous black material having a brilliant vitreous luster, (2) grayish black, less brilliant, striated material usually of silky luster, and (3) generally thinner bands or lenses of soft, powdery, and fibrous particles of mineral charcoal. The difference in luster of the bands is greater in bituminous than in subbituminous coal.

Splint Coal. A variety of bituminous or subbituminous coal, commonly having a dull luster and grayish black color, of compact structure, often containing a few thin irregu-

³⁹ Fisher, C. H., *Ind. Eng. Chem., Anal. Ed.*, **10**, 374-8 (1938).

⁴⁰ Seyler, C. A., *Colliery Guardian*, **155**, 990-4, 1046-8, 1087-9, 1137-9, 1231-3 (1937); *Proc. S. Wales Inst. Engrs.*, **53**, 254-327, 396-407 (1938); *Fuel*, **17**, 177-86, 200-9, 235-42 (1938).

⁴¹ *Am. Soc. Testing Materials, Sectional Comm. on Classification Coal, Gen. Circ.* **59**, p. 1, 1936.

⁴² *Am. Soc. Testing Materials, Standards*, Pt. III, p. 58, 1939.

lar bands with vitreous luster. When struck, it is resonant. It is hard and tough and breaks with an irregular, rough, sometimes splintery fracture. It is free burning and does not swell on heating.

Cannel Coal. A variety of bituminous or subbituminous coal of uniform and compact fine-grained texture with a general absence of banded structure. It is dark gray to black in color, has a greasy luster, and is noticeably of conchoidal or shell-like fracture. It is noncaking, yields a high percentage of volatile matter, ignites easily, and burns with a luminous, smoky flame.

Boghead Coal. A variety of bituminous or subbituminous coal resembling cannel coal in appearance and behavior during combustion. It is characterized by a high percentage of algal remains and volatile matter. Upon distillation it gives exceptionally high yields of tar and oil.

Equivalent differences exist in the plant constituents from which lignitic and anthracitic coals were derived, but there is less need for commercial definitions of such varieties in the United States at the present time. A German industry has been built upon the recovery of products from certain "brown coals," which are canneloid coals of lignitic rank. In anthracite, the various layers and petrologic constituents have been so greatly altered by devolatilization, pressure, etc., that the remaining differences are much less apparent, and of less practical importance, than in bituminous coal.

White⁴³ has suggested a plan of classification which provides for coals of each type, in several ranks beginning with peat.

The commercial varieties of bituminous and subbituminous coal which are defined above represent types, since they result from differences in the proportion of the original plant constituents and their biochemical alteration products. It is not hard to identify *typical* samples of common

banded, splint, or cannel coals, but it must be remembered that commercial coals are often of intermediate and mixed character and thus harder to classify.

Common Banded Coal. As indicated in Tables IV and V, common banded or bright coals may be high in either anthraxylon or translucent attritus, and their properties will vary accordingly. The following classes have been recognized, according to the predominant plant remains: humic, spore, resinous, cuticle, leaf, and bark coals.²⁰

Splint and Semisplint Coals. These are predominantly attrital coals, being characterized by opaque or semiopaque attritus in coals of bituminous rank. They likewise vary considerably according to the percentage of different plant constituents which are present.^{20, 33, 44}

Cannel Coal. Ashley⁴⁵ has described the occurrence and general characteristics of the cannel coals of the United States. At present there is no comprehensive publication on the petrologic nature of the cannel coals of this country, but they are known to be extremely variable. White and Thiessen⁴⁶ have discussed canneloid coals of lignitic, subbituminous, and bituminous ranks from several United States localities. A paper by U. S. Bureau of Mines authors³⁴ gives the proximate, ultimate, and petrographic analyses of nineteen samples used for hydrogenation tests, of which seven were designated as cannels and two as intermediate between cannel and boghead coal. Cannels which are similar in physical properties may vary considerably in chemical properties, de-

⁴⁴ Thiessen, R., *ibid.*, 88, 644-71 (1930). Stopes, M. C., and Wheeler, R. V., *Fuel*, 3, 439-52 (1924). Stopes, M. C., *ibid.*, 14, 4-13 (1935).

⁴⁵ Ashley, G. H., *U. S. Geol. Survey, Bull.* 659 (1918), 127 pp.

⁴³ White, D., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 517-26 (1930).

⁴⁶ White, D., and Thiessen, R., *U. S. Bur. Mines, Bull.* 38 (1913), 390 pp.

pending upon whether they are the spore or woody varieties of cannel.

Bode⁴⁷ has discussed methods for distinguishing between cannel and the more highly coalified pseudocannel coals, also bogheads and bituminous shales.

Boghead Coal. Thiessen has discussed the origin of boghead or algal coals, mostly with reference to foreign samples. However, mention is made of coals of this type from Kentucky, Pennsylvania, and Alaska.²⁴ Stadnikoff has presented considerable data on the properties of tar fractions from Siberian bogheads, also the nature of extracts and hydrogenation products.⁴⁸ He distinguished bogheads from other bituminous coals by the boghead's very great yield of low-temperature tar which is almost free from phenols (1 or 2 percent), and the small amount of bitumen extractable with solvents. In comparison, humic bituminous coals give a low-temperature tar which is very rich in phenols, and a relatively large yield of bitumen by extraction. Karavaev⁴⁹ has also presented data on the behavior of boghead coal towards solvents and reagents, and the distillation yields and properties of tar fractions.

COMMERCIAL AVAILABILITY OF COAL TYPES

Many coal seams consist predominantly of a single one of the coal types which have been described. In other seams, the upper and lower parts may be sufficiently different in type and grade or purity to justify loading the two parts of the seam separately and selling them for different uses. Common or bright coals are by far the most abundant, but splint and semi-splint or block coals have well-established

markets. The tonnage production of cannel and boghead coals in the United States is small.

Many of the commercially important coal seams of the United States contain a mixture of two or more coal types. When bituminous coal is screened into sizes, there is often an appreciable concentration of types in the various portions. For example, splint and cannel layers are tough and tend to remain in the largest sizes. Bright coal, especially the anthraxylon or vitrain, is more brittle and tends to be fractured in the bed even before mining, so that it is found especially in the intermediate sizes. The fusain or mineral charcoal, which rubs off in handling, tends to concentrate in the dust. McCabe, Konzo, and Rees⁵⁰ prepared high-vitrain, high-clarain, and high-durain samples for stoker tests, from the $\frac{7}{16}$ -inch by 10 mesh, 3-inch by 2-inch, and the 6-inch by 3-inch fractions respectively, produced at an Illinois coal mine.

Selective mining, handpicking, screening, special crushing, gravity or froth flotation, hydrogenation, and other methods may be used to produce coal fractions which are richer than the average in particular constituents. None of these methods are very efficient for the separation of coal constituents, and they are seldom used commercially for the specific purpose of separating coal types or components. However, the products of such treatments may differ usefully from each other, and from the original mixture, because of partial separation of the banded constituents. For example, it has been reported that the fines obtained by dedusting a high-volatile Illinois bituminous coal are sufficiently

⁴⁷ Bode, H., *Glückauf*, **67**, 1245-51 (1931).

⁴⁸ Stadnikoff, G. L., *Proc. 2nd Intern. Conf. Bituminous Coal*, **1**, 608-24, 625-31 (1928).

⁴⁹ Karavaev, N. M., *Fuel*, **13**, 299-310 (1934).

⁵⁰ McCabe, L. C., Konzo, S., and Rees, O. W., *Illinois State Geol. Survey, Rept. Investigations* **78** (1942), 14 pp.

high in fusain to produce a "commercially smokeless" briquet.⁵¹

Lehmann and Hoffmann⁵² proposed the controlled crushing of coal by elastic percussion in a beater mill to concentrate the dull coal in the coarse granules, the bright coal in the intermediate size, and the fusain in the dust. Fieldner and Rice⁵³ reported quantitative figures on the energy required to pulverize the four constituents of an Illinois coal to minus 150 mesh. The energy ranged from 1.8 horsepower-hours per ton for fusain to 13.6 for durain.

Lehmann and Hoffmann⁵² determined the percentage of each type of coal in the various granulated sizes by embedding the coal in a cementing medium, polishing the specimen, and examining by reflected light. The petrographic details of grain formation, reflecting properties, color, and relief were used to identify the constituents and to estimate the proportion of each. Kühlwein and Demann have discussed industrial experiences and fundamental difficulties in the petrographical analysis of pulverized coal.⁵⁴

Small-scale hydrogenation tests on the banded constituents of coals have shown that these constituents vary considerably in ease of liquefaction.⁵³ In coals containing less than 89 percent carbon on the dry, ash-free basis, the easily liquefiable constituents included anthraxylon and all organic constituents of the translucent attritus, such as woody degradation matter, leaves, spores, pollens, cuticles, resins, and algae. Under specified hydrogenation conditions, the average liquefaction yield from

12 splint samples was 39 to 79 percent, and the yield from 7 samples of fusain was only 15 to 27 percent.

CLASSIFICATION BY RANK

The rank of coal is its stage of coalification in the series peat, lignite, subbituminous coal, bituminous coal, and anthracite. The generally accepted theory, which originated with von Beroldingen⁵⁵ in 1778, is that the various ranks of common coal have resulted from peat deposits which were covered with layers of sedimentary rock and have been coalified to varying degrees by tremendous pressures acting through long periods of time, supplemented by the effect of moderate heat in coals of the highest ranks.

EFFECT OF COAL TYPE ON RANK CLASSIFICATION

Many methods have been proposed for determining the rank of coals, and the exact definition of rank will therefore depend on the criteria selected. Regardless of what chemical or physical factors are used, differences will be found when examining the banded constituents of a single sample, due to differences in plant residues when the dynamochemical process of coalification began. Thus it was seen in Table VIII that the petrographic constituents of a certain seam gave volatile-matter yields ranging from 19.8 to 42.1 percent. These constituents, when isolated, would fall into different ranks by almost any system of classification, in spite of the fact that presumably they have all been subjected to similar pressure and temperature conditions during coalification.

This apparent paradox is merely a mat-

⁵¹ Fieldner, A. C., *Mining and Met.*, **23**, 103-4 (1942).

⁵² Lehmann, K., and Hoffmann, E., *Brennstoff-Chem.*, **13**, 21-9 (1932); *Fuel*, **13**, 271-8 (1934).

⁵³ Fieldner, A. C., and Rice, W. E., *U. S. Bur. Mines, Information Circ.* **7143** (1941), 50 pp.

⁵⁴ Kühlwein, F. L., *Glückauf*, **67**, 1124-6 (1931). Demann, W., *ibid.*, **67**, 1128-9 (1931).

⁵⁵ Von Beroldingen, F., *Beobachtungen, Zweifel und Fragen, die Mineralogie überhaupt und insbesondere ein natürliches Mineral System betreffend*, Hannover, 1st ed., 1778, 203 pp.; 2nd ed., 1792, Vol. I.

ter of definition. For practical purposes it is sufficient to consider the properties of coals as they now exist, without reference to theories concerning their formation. Practical classification is based on the average properties of coals as they are produced or used. If the coal from a given seam is separated in practice into two or more portions which vary in nature, it is not only permissible but even necessary to classify them separately. Thus, in the practical sense, the rank of a coal is determined and defined by whatever criteria are arbitrarily used for classification, and the geological concept of rank serves merely as a useful generalization.

Rose⁵⁶ in discussing the classification of coals by ultimate analysis, in 1930, pointed out that the composite nature of coal adds to the difficulty but usually does not prevent satisfactory coal classification on a chemical basis.

For scientific purposes, when it is desired to compare accurately the degree of coalification of various coals, the properties of the anthraxylon (vitrain) may be determined and compared as a measure of rank. Most coals except cannel and bog-head contain layers of this constituent which can be separated in fairly pure condition in quantities sufficient for analysis. Being derived from woody tissue, it furnishes a fairly consistent and definite constituent in most coals, as compared with the extremely variable attrital matter.

Francis⁵⁷ preferred to use vitrain for determining the rank of coal by oxidizability of the coal ulmins. Seyler⁴⁰ stated, ". . . for the present we can only judge the rank of a coal accurately from the

vitrain associated with it." McCabe⁵⁸ has used vitrain in a study of physical properties of fifteen samples of bituminous and subbituminous coals and lignite. Fisher and coworkers,⁵⁹ who have studied the hydrogenation of anthraxylon (vitrain) from peat, brown coal, lignite, subbituminous coal, bituminous coal, and anthracite, have presented a graph showing that there is a linear relationship between carbon and oxygen for anthraxylon from all these coals as well as for wood and cotton. In other words, this petrographic constituent has a fairly definite composition at each carbon content (rank).

PROGRESSIVE COALIFICATION

The geological age of a coal deposit does not determine the rank of the coal. For example, some coals of the Carboniferous Age have never been subjected to much pressure or temperature and are still of lignitic rank, whereas much younger deposits of the Tertiary Age have been locally altered into bituminous coal or even anthracite.

The causes and effects of the geological alteration of coal to higher ranks have long interested geologists and chemists in many countries, and there is an extensive literature on this subject.

White,³⁷ in discussing the progressive regional carbonization of coal, presented diagrams showing the change in carbon, hydrogen, and oxygen contents, beginning with the source materials of coals and ending with anthracite and graphite. Separate curves were given for common (xyloid or woody) coal, cannels, and algal or bog-head coals. He considered that the chemical composition of these types converges

⁵⁶ Rose, H. J., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 411-4 (1930).

⁵⁷ Francis, W., *J. Inst. Fuel*, 6, 301-13 (1933).

⁵⁸ McCabe, L. C., *Fuel*, 16, 267-80, 309-16 (1937).

⁵⁹ Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., Fein, M. L., and Storch, H. H., *ibid.*, 19, 132-8, 162-72 (1940).

in the low-volatile bituminous rank. Briggs⁶⁰ has graphed analyses showing the development in rank of a variety of carbonaceous materials including not only the several types of coals but also coal constituents.

Campbell⁶¹ has presented a general discussion of characteristic stages which can be recognized in the metamorphism of coal, six of which occur before there is any appreciable alteration in the associated rocks. Stadnichenko⁶² has compared the proximate and ultimate analyses and petrographic composition of a series of bituminous coal samples from the Lower Kittanning Seam in western Pennsylvania, ranging from 58.6 to 84.7 percent fixed carbon. This bed passes horizontally, almost without folding, from one side to the other of a great syncline, where no effect from igneous intrusions is known to exist. The author concluded that the thrust pressure theory furnishes the only satisfactory explanation of the changes in rank of this coal bed.

McFarlane and Dapples have discussed the effect of igneous metamorphism on low-rank bituminous or subbituminous coals which have been altered locally to semianthracite, anthracite, or natural coke in two different areas of Colorado.⁶³ These papers contain information on the effect of thickness of the igneous intrusion and distance from the coal seams upon the degree of alteration as shown by proximate analyses and specific gravity. Estimates were made of the temperatures which were reached in the various samples. Dapples's paper used the A.S.T.M. coal classification

terminology, and it contains information on petrographic constituents. Dapples reviewed many theories of coal metamorphism resulting from heat and pressure, with references to the original papers. He concluded that both temperatures from 300 to 350° C and pressures of the order of 1,400 to 2,800 atmospheres are necessary for anthracitization. He believed that, where heat is not available from igneous sources, it has been derived from frictional heat resulting from shearing due to countless small movements.

Kreulen⁶⁴ has discussed the analysis and calorific value of samples from a deposit which ranges from lignite to natural coke.

MANY CRITERIA PROPOSED FOR RANK CLASSIFICATION

It has been shown by many investigators that there is persistent microstructure in the series peat to anthracite, as well as a continuous transition in chemical and physical properties. Almost any one of these properties, or any combination of them, can be used for classifying coals according to rank, but certain ones are more satisfactory and practical than others.

The best-known systems of classification according to rank are based either on proximate analysis (volatile matter or fixed carbon) and calorific value, or on ultimate analysis (carbon, hydrogen, and oxygen). As will be shown later, a good degree of correlation can be established between these two methods, and the best system is largely a matter of expediency.

A great many systems of classification based on these factors have been proposed, many of which have been subject to later revision by their authors or others, and most of them have become obsolete or survive only in much altered form. A com-

⁶⁰ Briggs, H., *Proc. Roy. Soc. Edinburgh*, **52**, Pt. 2, 195-9 (1932).

⁶¹ Campbell, M. R., *Econ. Geol.*, **25**, 675-96 (1930).

⁶² Stadnichenko, T., *ibid.*, **29**, 511-43 (1934).

⁶³ McFarlane, G. C., *Econ. Geol.*, **24**, 1-14 (1929). Dapples, E. C., *ibid.*, **34**, 369-98 (1939).

⁶⁴ Kreulen, D. J. W., *Chem. Weekblad*, **30**, 387-91 (1933).

prehensive history of the progress of coal classification during the past hundred years would hardly justify the space required for presentation.

CLASSIFICATION BY ULTIMATE ANALYSIS

The ultimate analysis has appeared to many chemists to be the most fundamental and therefore the most desirable basis for classifying coals. Six items are included in the conventional analysis, namely: carbon, hydrogen, oxygen, nitrogen, sulfur, and ash. The usual objective is to obtain the ultimate analysis of the "pure coal substance," free of variable mineral impurities (termed "ash" after ignition) and moisture. For classification purposes, ultimate analyses are usually calculated to the dry, ash-free basis before use, and sulfur and nitrogen may also be eliminated. Such recalculated analyses do not approximate the analysis of pure coal substance as closely as was formerly supposed, for reasons which will be discussed later. Oxygen is nearly always determined by difference and is therefore subject to the summation of errors of the other five constituents. In some analyses oxygen and nitrogen have been estimated jointly by difference.

As early as 1826, Karsten⁶⁵ had classified bituminous coals on the appearance of the coke residue, and he attributed special significance to the ratio of hydrogen to oxygen in relation to coking power.

Regnault-Gruner Classification. The first fairly accurate ultimate analyses of coals were made by Regnault,^{66, 67} who in 1837 published the ultimate analyses of coals of various ranks from many parts of

the world. The primary arrangement of coals in his tables was according to geological eras and the relative position of seams in the coal-bearing strata. The identifying names used included the following:

Anthracites.

Houilles grasses et dures (coals fat and hard).

Houilles grasses maréchales (fat smithing).

Houilles grasses à longue flamme (fat long flame).

Houilles sèches à longue flamme (dry long flame).

Jayet (jet).

Lignite parfait.

Lignite imparfait.

Charbon roux (brown coal).

Tourbe (peat).

Bois (wood).

Regnault's tables gave carbon, hydrogen, and oxygen plus nitrogen, both as determined and as calculated to the ash-free basis, the nature of the coke obtained and its yield on the ash-free basis (i.e., fixed carbon), also the density of the various coals.

From his studies, Regnault concluded that coals of similar qualities had similar ultimate analyses, and he decided that the percentage of oxygen plus nitrogen was a good indication of their nature. Although Regnault presented the analyses of various coals of each rank, definite limits for the groups were not set up until nearly forty years later by L. Gruner,⁶⁸ who gave a table of ultimate analysis limits for bituminous coals, and who ended his paper with a table summarizing volatile matter, fixed carbon, coke quality, and calorific-value limits for the same classes. In 1911, E. Gruner and Bousquet⁶⁹ quoted the same numerical values (except for typo-

⁶⁵ Karsten, C. J. B., *Karsten's Archiv Bergbau*, 12, 3-244 (1826).

⁶⁶ Regnault, V., *Ann. chim. phys.*, [2] 66, 337-65 (1837).

⁶⁷ Regnault, V., *Ann. mines*, [3] 12, 161-240 (1837).

⁶⁸ Gruner, L., *Ann. mines*, [7] 4, 169-207 (1874) [1873].

⁶⁹ Gruner, E., and Bousquet, G., p. 16 of ref. 5.

graphical errors) in a book published by the central committee of French collieries. These authors stated that the classification of coal is based on the proportion of volatile matter and the nature of coke, and the ultimate analysis limits were cited but given a secondary position. These limits are given in Table XI and have been shown graphically by Rose.⁵⁶

Seyler's Classification. Seyler^{72, 73} published what has developed into the outstanding system of classification based on ultimate analysis. This originated principally from a consideration of the coals of South Wales, but in 1924 Seyler⁷⁴ published his classification with a large number of British and European coal analyses as supporting data. The percentages of

TABLE XI

ULTIMATE ANALYSIS LIMITS ACCORDING TO GRUNER AND BOUSQUET¹

Class or Type of Coal	Carbon percent	Hydrogen percent	Oxygen and Nitrogen percent	Ratio O + N H
1. Houilles sèches à longue flamme	75-80	5.5-4.5	19.5-15.5	Between 4 and 3
2. Houilles grasses à longue flamme	80-85	5.8-5.0	14.2-10.0	Between 3 and 2
3. Houilles grasses proprement dites	84-89	5.0-5.5	11.0-5.5	Between 2 and 1
4. Houilles grasses à courte flamme	88-91	5.5-4.5	6.5-4.5	About 1
5. Houilles maigres ou anthraciteuses	90-93	4.5-4.0	5.5-3.0	Less than 1
6. Anthracites	93-95	4.0-2.0	3.0	1-0.5

German Use of Ultimate Analysis. Stein⁷⁰ in 1857 concluded that ultimate analysis taught nothing as to the true value of coal, but the analyses which he used appear to have been erroneous. His pupil Fleck⁷¹ attempted a classification based on what he called the available hydrogen, that is, the hydrogen in excess of the amount required to combine with all the oxygen in the coal. The available-hydrogen concept does not represent the facts and has long been almost obsolete. However, the idea has been extensively cited, and modern authors sometimes show "available hydrogen" in tables or graphs for comparison with other data.

⁷⁰ Stein, W., *Berg- u. hüttenmänn. Ztg.*, **16**, 382-5, 399-400 (1857).

⁷¹ Geinitz, H. B., Fleck, H., and Hartig, E., *Über die Steinkohlen Deutschlands*, Oldenbourg, Munich, 1865, Vol. 2, 428 pp. Fleck, H., *Dinglers Polytech. J.*, **180**, 460-71 (1866), **181**, 48-57, 267-83 (1866), **195**, 430-48 (1870).

carbon, hydrogen, and oxygen plus nitrogen on the dry, ash- and sulfur-free basis were included, together with the volatile matter. Frequently, comments were made on the bitumen index, caking properties, coke quality, or industrial uses of the samples.

Seyler pointed out in his original paper that coals of the same carbon content may have high, normal, or low hydrogen contents, so that long-, normal-, and short-flame coals are not confined to the carbon limits stated by Gruner.

Seyler's classification is presented in summarized form in Table XII, in which the lowest-rank coals are at the right and highest-rank coals are at the left. The

⁷² Seyler, C. A., *Proc. S. Wales Inst. Engrs.*, **21**, 483-526 (1899), **22**, 112-20 (1900).

⁷³ Seyler, C. A., *Colliery Guardian*, **80**, 17-9, 80-2, 134-6 (1900).

⁷⁴ Seyler, C. A., *Fuel*, **3**, 15-26, 41-9, 79-83 (1924).

SEYLER'S CLASSIFICATION

classification is based on carbon and hydrogen percentages. The nomenclature is intended to be systematic and descriptive; it seems formidable at first acquaintance and is confusing in several respects until one has considerable familiarity with the system.

It will be seen from Table XII that coals are classified according to their carbon content into seven vertical columns, which Seyler calls "carbon planes" and which have a range from 2 to 5 percent in carbon content. The horizontal divisions represent "hydrogen planes" or genera having similar but not identical hydrogen limits at different carbon contents. The range of hydrogen percentage is small in these genera, being as low as 0.25 percent in one genus. The intersections of the carbon and hydrogen limits produce a series of areas containing similar coals, known as "species."

In each vertical carbon column, one or two species is considered to represent the normal coal of that carbon content, and is shown in the table in small capitals. These coals may be distinguished by the prefix "ortho," meaning true, typical, or normal. Coals in the same column with more hydrogen are called "per-hydrous," which may be shortened to the prefix "per," and coals with less hydrogen are "sub-hydrous," which is shortened to the prefix "sub." Since there may be as many as three species in the same carbon range with less than normal hydrogen content, the prefix "sub" is not sufficient, and the less typical species are further identified by the prefix "pseudo" combined with the name of an adjoining carbon classification.

For high-rank coals of higher than normal hydrogen content, the prefix "semi" or "pseudo" is used in connection with the name of an adjoining species. It should be pointed out that Seyler's use of the

term "subbituminous" to mean coal of lower than normal hydrogen and volatile matter is quite different from American usage for this term, which will be defined later.

The confusing aspect of Seyler's nomenclature is partly due to the multiplicity of terms, to the exceptions in his method of assigning names, and to the fact that the prefixes "ortho" and "pseudo" are each used to indicate deviations from the normal in two different directions. This requires a double set of names, and multiple prefixes, for most of the nontypical coals, the designations sometimes running as high as fourteen syllables. His normal or common "species" have shorter names. Seyler⁷⁵ pointed out the possibility of designating coals simply by their carbon and hydrogen percentage, like locating geographical points by stating latitude and longitude. He also made extensive use of the carbon-to-hydrogen ratio.

Seyler's classification, together with the large amount of supplementary information which he has published on the correlation of ultimate analyses with petrologic constituents, volatile matter, calorific value, caking and combustion properties, etc., has been a most valuable contribution to the scientific classification of coal. The classification of the lowest-rank coals, with which Seyler has had little familiarity, is inadequate. The classification of anthracite as shown in Table XII is also inadequate, but Seyler has further classified the anthracites of South Wales.⁷⁶ He does not provide for the hard, low-volatile anthracites which are produced in large tonnages elsewhere.

The Midland Coke Research Commit-

⁷⁵ Seyler, C. A., *Proc. S. Wales Inst. Engrs.*, **47**, 557-92 (1931).

⁷⁶ Davies, D. F., *ibid.*, **48**, 4-39 (1932).

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TABLE XII

SEYLER'S CLASSIFICATION ⁷⁴

Analyses calculated to the dry, ash- and sulfur-free basis

Genus	Anthracitic	Carbonaceous	Bituminous			Lignitous	
			Meta-	Ortho-	Para-	Meta-	Ortho-
	Over 93.3% C	93.3-91.2% C	91.2-89.0% C	89.0-87.0% C	87.0-84.0% C	84-80% C	80-75% C
Perbituminous	Perbituminous (per-meta-bituminous) Over 5.7% H 30-44% V.M.	Perbituminous (per-ortho-bituminous) 5.7% H and over Over 36% V.M.	Perbituminous (per-para-bituminous) Over 5.8% H Over 40% V.M.	Periglignitous	
Bituminous	(Pseudobituminous species)	Meta-BITUMINOUS 4.9-5.7% H 23-30% V.M.	ORTHO-BITUMINOUS 5.0-5.7% H 23-30% V.M.	PARA-BITUMINOUS 5.0-5.8% H 30-40% V.M.	LIGNITOUS (meta-) 5.8% H 31-57% V.M.	
Semibituminous	SEMIBITUMINOUS species (ortho-semibituminous) Over 4.45% H 14-24% V.M.	Subbituminous (sub-meta-bituminous) 4.5-4.8% H 16-23% V.M.	Subbituminous (sub-ortho-bituminous) 4.5-5.0% H 16-23% V.M.	Subbituminous (sub-para-bituminous) 5.0% H and under 16-28% V.M.	Sublignitous (meta-)	
Carbonaceous	Semianthracitic species Over 4% H 9-15% V.M.	CARBONACEOUS species (ortho-carbonaceous) 4.2-4.45% H 10-14% V.M.	Pseudocarbonaceous (sub-meta-bituminous) 3.7-4.5% H 10-16% V.M.	Pseudocarbonaceous (sub-ortho-bituminous) Under 4.5% H Under 16% V.M.	Pseudocarbonaceous (sub-para-bituminous)	
Anthracitic	ORTHO-ANTHRACITE (true anthracite) Under 4% H 5-9% V.M.	Pseudoanthracite (subcarbonaceous) Under 4.2% H Subcarb. = 7.7-12% V.M. Pseudoanthr. = under 7.7% V.M.	Pseudoanthracite (sub-meta-bituminous) Under 3.7% H Under 10% V.M.	Pseudoanthracite (sub-ortho-bituminous)	Pseudoanthracite (sub-para-bituminous)	

H = hydrogen ; C = carbon ; V.M. = volatile matter.

tee,⁷⁷ after a study of the classification of coals for coke making, concluded that:

... Seyler's classification of coal requires reconsideration, not only in the limits given for different types but, in particular, to extend the lower limit of the range of bituminous coals from 84 to 80 per cent. carbon.

Seyler's conception of coal species of higher or lower than normal hydrogen content was originally empirical, representing observed differences in general type, but he has since correlated them with petrologic composition,⁴⁰ with graphs correlating the percentages of hydrogen, carbon, and volatile matter in vitrain (anthraxylon) of various ranks. Bright coals rich in this constituent have the normal hydrogen content for each rank. By the U. S. Bureau of Mines terminology described earlier in this chapter, the coals of higher hydrogen content are rich in material derived from resins, waxes, spore and pollen exines, cuticles, or algae, while the lower-hydrogen coals of the same carbon content are rich in fusain or opaque attritus.

Kent⁷⁸ has described certain low-hydrogen coals of subbituminous or lignitic rank from Western Australia. The characteristics of these coals were attributed to an unusually high percentage of fusain, which, however, was not estimated.

In 1928, Seyler^{79, 80} presented the case for classification of coal by ultimate analysis as compared with proximate analysis and Btu. A graph correlates his classification with those of Parr⁸¹ and Ralston,⁸²

which are to be described later in this chapter.

Seyler has discussed coal classification as applied to fuel technology and the influence of petrologic constituents, in several papers not previously mentioned.^{83, 84} The last reference contains a large folded chart correlating the Seyler classification according to carbon and hydrogen content, with volatile matter, moisture, gross and net calorific value, volume of wet flue gas, theoretical air required, calorific intensity, and flame intensity. This chart includes wood and vegetable matter, peat, and lignite of three classifications, as well as the higher-rank coals. The paper has also appeared elsewhere in whole or in part.⁸⁵

Seyler's classification has been used by some English coal investigators, but it apparently has not received widespread acceptance for either research or commercial purposes. However, it is sound in conception and well documented, and it is the outstanding classification based on ultimate analysis.

American Use of Ultimate Analysis. Rogers⁸⁶ included ultimate analyses in a classification of Pennsylvania coals into four groups.

Grout⁸⁷ in 1907 recalculated ultimate analyses of dry fuels to the basis of carbon plus hydrogen plus oxygen equals 100 per cent and graphed them on a triaxial diagram. He found that points representing

⁸³ Seyler, C. A., *Proc. World Eng. Congr., Tokyo, 1929*, **32**, 271-85 (1931).

⁸⁴ Seyler, C. A., *Proc. S. Wales Inst. Engrs.*, **47**, 4-9, 549-55, 557-92, 607-16, 685-94, 746-59 (1931).

⁸⁵ Seyler, C. A., *Colliery Guardian*, **142**, 401-4, 488-90, 577-9 (1931); *Gas World*, Ann. Coal Suppl., **94**, 23-4 (1931); *J. Inst. Fuel*, **4**, 451-6 (1931); *Iron & Coal Trades Rev.*, **122**, 836, 860, 898-900 (1931).

⁸⁶ Rogers, H. D., *The Geology of Pennsylvania, a Government Survey*, J. B. Lippincott & Co., Philadelphia, 1858, Vol. 2, pp. 988-97.

⁸⁷ Grout, F. F., *Econ. Geol.*, **2**, 225-41 (1907).

⁷⁷ Anon., *Fuel*, **20**, 156-9 (1941).

⁷⁸ Kent, C. R., *Fuel*, **19**, 119-25 (1940).

⁷⁹ Seyler, C. A., *Trans. Am. Inst. Mining Met. Engrs.*, **76**, 189-96 (1928).

⁸⁰ Seyler, C. A., *J. Inst. Fuel*, **5**, 248-55 (1932).

⁸¹ Parr, S. W., *J. Ind. Eng. Chem.*, **14**, 919-23 (1922).

⁸² Ralston, O. C., *U. S. Bur. Mines, Tech. Paper* **93** (1915), 41 pp.

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the natural series, wood to anthracite, formed a narrow band on the diagram, but that cannel coals, being high in hydrogen, fell above the band of ordinary coals. Grout showed that lines could be drawn on the diagram to separate coals of similar calorific value. He proposed a classification based on dry, ash-free analyses, which involved both fixed carbon (that is, 100 minus percentage of volatile matter) and total carbon from the ultimate analysis.

White⁸⁸ studied the effect of oxygen in coal, and he concluded that it has approximately the same effect as ash on the calorific value. He obtained a smooth curve by plotting the calorific value against the ratio of carbon divided by (oxygen plus ash). The greatest deviations were for weathered or high-rank coals. He concluded that the carbon-to-oxygen ratio marked the degree of coalification, and that the hydrogen-to-oxygen ratio gave a fairly good indication of coking property, except for high-rank coals.

Ralston⁸² in 1915 systematically extended Grout's proposals by recalculating 3,000 government analyses of coals and allied materials, deriving a number of useful generalizations which were shown on graphs. These included the location of isocalorific and isovolatilic lines on the ultimate analysis diagram, and the effect of carbonization and oxidation upon coal analyses. Ralston also graphed the analyses of resins, tars, waxes, fats, and oils. He concluded that the spread of analyses across the coal band (range of hydrogen percentage at the same carbon content) was greater than the probable analytical error and therefore represented real differences, which are now known to be due to differences in "type."

⁸⁸ White, D., *U. S. Geol. Survey, Bull.* 382 (1909), 74 pp.

Ralston found that, when coals were classified according to the practice of the U. S. Geological Survey, the various named classes fell on different parts of the coal band, with only a little overlapping of ultimate analyses. He did not propose definite limits for the various classes.

Drakeley and Smith⁸⁹ in 1922 published a graphic study, according to the methods of Grout and Ralston, of 287 British coals, and reached about the same conclusions as the previous investigators working with coals of the United States. Hickling⁹⁰ has graphed United States coal analyses in a similar manner.

Ultimate Analysis Ratios. Ratios of the various elements have been used since the earliest attempts at coal classification. Reference has already been made to Karsten's use of the hydrogen-to-oxygen ratio in 1826 and Regnault's use of the reverse ratio in 1837. The carbon-to-hydrogen ratio has been extensively employed by investigators working with the higher-rank coals, for example by Seyler and by Campbell.⁹¹ Strahan and Pollard⁹² used this ratio in the study of progressive anthracitization of the coal seams of South Wales. Bode⁹³ has proposed carbon-to-hydrogen ratio limits of 8 to 10 for boghead, 10 to 14 for cannel, and 14 to 18 for pseudo-cannel. White's use of the carbon-to-oxygen ratio has already been cited.

The significance and limitations of these ratios do not seem to have been fully

⁸⁹ Drakeley, T. J., and Smith, F. W., *J. Chem. Soc.*, 121, 221-38 (1922). Drakeley, T. J., *Fuel*, 2, 195-200 (1923).

⁹⁰ Hickling, G., *Trans. North Engl. Inst. Mining Mech. Engrs.*, 77, 25-45 (1927); *Colliery Guardian*, 133, 1049-50 (1927).

⁹¹ Campbell, M. R., *Trans. Am. Inst. Mining Met. Engrs.*, 36, 324-40 (1906).

⁹² Strahan, A., and Pollard, W., *Mem. Geol. Survey, England and Wales*, London, 1908, pp. 1-78.

⁹³ Bode, H., *Proc. 3rd Intern. Conf. Bituminous Coal*, 2, 878-96 (1931).

realized by all who have used them. The ratios have been graphically shown by Rose.⁹⁴

Figure 1, adapted by Rose from Ralston, shows the approximate limits of ultimate analysis of common varieties of United States coals on the dry basis, using the terminology most generally accepted at that time. It will be seen that this figure

bon-to-oxygen ratios, respectively, superimposed on the band of typical coal analyses. These figures show the obvious limitations of such ratios when they are applied to coals of all ranks.

Thus in Fig. 2 the hydrogen-to-oxygen ratios cut across the band of lower-rank coals, though more obliquely than the oxygen lines, but for the high-rank coals the

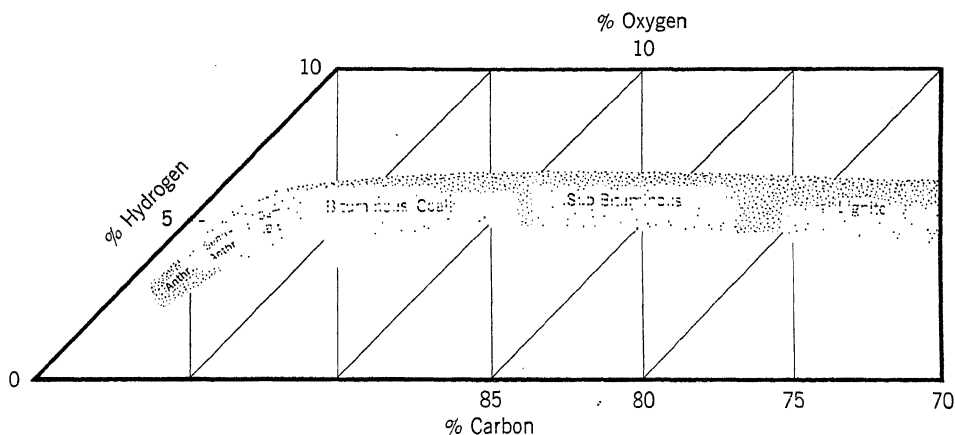


FIG. 1. Triaxial diagram of coal ultimate analyses, showing former U.S. Geological Survey terminology.

represents one corner from a triaxial diagram on which carbon plus hydrogen plus oxygen equals 100 percent. When the ultimate analyses of common types of solid fuels, not including cannel and algal coals, are plotted on this diagram, the analyses fall within a narrow band. The stippling on this figure does not represent actual coal analyses but merely indicates the limits within which the analyses of most coals will fall.

Figures 2, 3, and 4 show the hydrogen-to-oxygen, carbon-to-hydrogen, and car-

ratio lines run *parallel* with the coal band. The 150 ratio line passes through the four highest ranks of coal, from anthracite to bituminous, and would also pass through the cannel and algal coal areas if they were shown. Obviously this ratio is of little value for separating the high-rank coals. This figure also shows the line of zero "available hydrogen" and illustrates that the "available hydrogen" is highest with the coking, bituminous and semibituminous, coals and least with the noncoking lignites and anthracites. In other words, there is a broad correlation between the numerical values for available hydrogen and coking power, in spite of the fact that this conception is of little value for specific coals.

⁹⁴ Rose, H. J., *Trans. Am. Inst. Mining Met. Engrs.*, **74**, 600-36 (1926); *Fuel*, **5**, 562 (1926), **6**, 41-6, 84-8 (1927); *Blast Furnace Steel Plant*, **14**, 344-9, 366, 390-5, 409, 423-5, 433 (1926); *Modern Mining*, **3**, 310, 340, 413 (1926); *Koppers Mitteilungen*, **10**, 65-102 (1928).

Figure 3 shows that the carbon-to-hydrogen ratio lines are not very different in slope from the horizontal hydrogen lines. This ratio has been used chiefly to differ-

lines found by Ralston.⁸² Volatile matter, or its complement, fixed carbon, has long been one of the most widely used items for classification purposes, and the utility of its

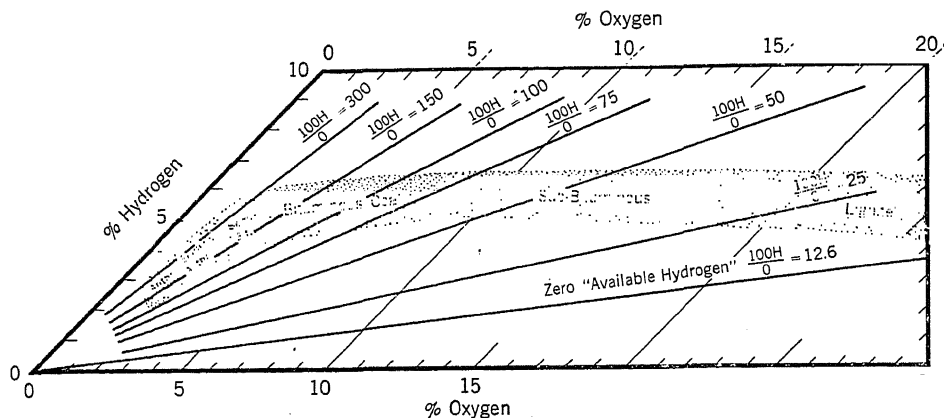


FIG. 2. Hydrogen-to-oxygen ratios graphed on triaxial diagram.

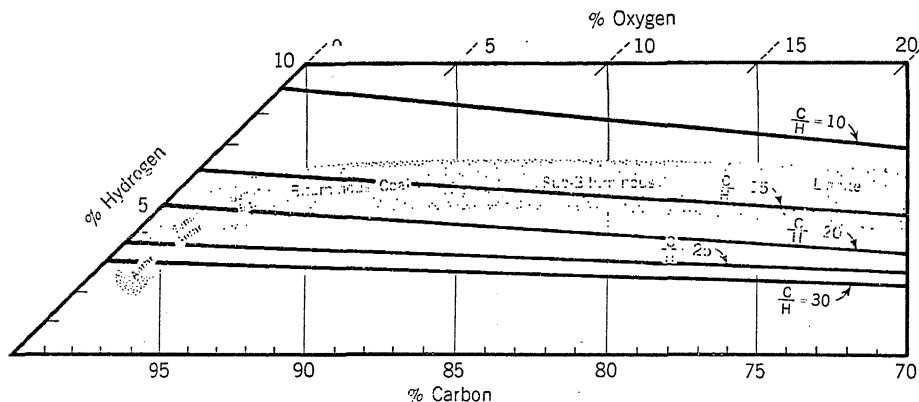


FIG. 3. Carbon-to-hydrogen ratios graphed on triaxial diagram.

entiate between high-rank coals. For coals of lower rank, this ratio runs nearly parallel with the coal band; for example, the 15 ratio passes completely through the bituminous, subbituminous, and lignite ranks, and the higher ratio lines cross the coal band only for high-rank coals.

However, the carbon-to-hydrogen ratio lines are nearly parallel with the isovolatile

approximate equivalent, the carbon-to-hydrogen ratio, for systems based on ultimate analysis may thus be understood. Seyler has also pointed out the equivalence of volatile matter and the carbon-to-hydrogen ratio.

Figure 4 shows that the slope of the carbon-to-oxygen ratio lines is so nearly that of the oxygen percentages that the

AVAILABILITY OF GOOD ULTIMATE ANALYSES

use of the oxygen percentage in pure coal should be about as satisfactory an index, and would be simpler to use and understand. The slope of the carbon-to-oxygen ratio lines is a little closer to that of the isocalorific lines but not near enough to be a practical equivalent. The correlation of calorific value and ultimate analysis will be discussed later. Regnault,⁶⁶ in 1837,

coke D271-37⁹⁵ state that the same laboratory, when testing portions from the same sample of 60-mesh coal, should obtain duplicate results differing not more than 0.3 percent for carbon and 0.07 percent for hydrogen. However, Lowry and Junge⁹⁶ have made a statistical study of duplicate ultimate analyses of coal reported by various fuel-testing laboratories.

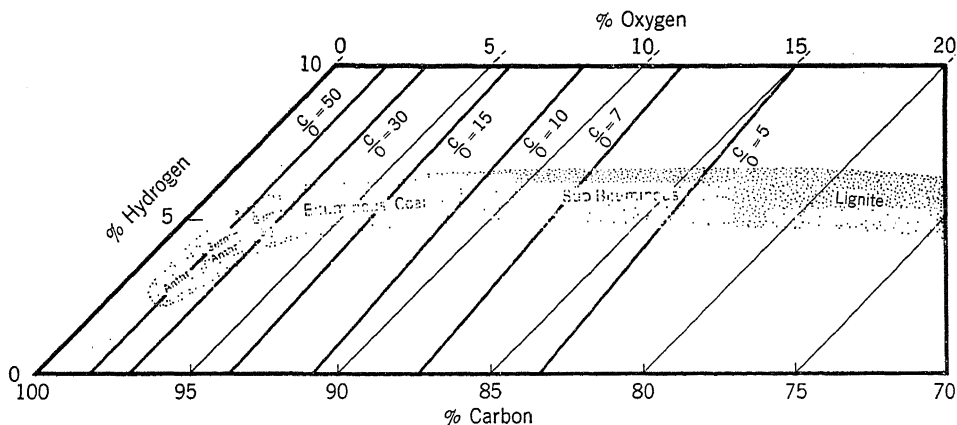


FIG. 4. Carbon-to-oxygen ratios graphed on triaxial diagram.

calculated the atomic ratio of hydrogen plus oxygen to carbon.

Availability of Good Ultimate Analyses. U. S. Bureau of Mines publications are the principal source of ultimate analyses of American coals. Such analyses are seldom made for industrial purposes in this country, except for calculating heat balances for boiler tests. Coal-research laboratories make a limited number of ultimate analyses in connection with the systematic investigation of the properties of coal. The necessary determinations require special equipment and skilled technique, and testing laboratories charge about \$25 for an ultimate analysis.

A.S.T.M. standard methods of laboratory sampling and analysis of coal and

On the basis of the analyses available, they concluded that a "reasonable" permissible difference between duplicate determinations by the same laboratory would be 0.5 percent for carbon and 0.15 percent for hydrogen. This merely represents the ability of the average analyst to get consistent results on the same sample; it does not represent the deviation from absolute accuracy, which would be considerably greater.

Tideswell and Wheeler⁹⁷ have doubted

⁹⁵ *Am. Soc. Testing Materials, Standards*, Pt. III, p. 15, 1939.

⁹⁶ Lowry, H. H., and Junge, C. O., Jr., *Am. Soc. Testing Materials, Preprint 80* (1942), 16 pp.

⁹⁷ Tideswell, F. V., and Wheeler, R. V., *Trans. Am. Inst. Mining Met. Engrs.*, **70**, 200-11 (1928).

that many published ultimate analyses of coals are accurate within 1 percent carbon, and they believe that many are as much as 2 or 3 percent in error. This is due in large part to the shaly, pyritic, and carbonate impurities in coal which lead to errors in the calculation of the composition of the pure coal substance on the ash-free basis. The errors can be reduced by making proper allowances for the changes which occur in these mineral impurities when they are incinerated to ash. Not only is the weight of ash different from the weight of the mineral impurities present in the coal, but also the water of hydration of shaly impurities and the carbon dioxide from carbonate impurities are commonly credited to the pure coal substance.

This is mentioned because ultimate analyses are sometimes considered to be more accurate for classification purposes than volatile matter or fixed carbon, which do not exist as such in the raw coal, and the yield of which depends somewhat on the particular test method used. Actually, both ultimate and proximate analyses are of acceptable accuracy for classification purposes, when corrected to the mineral-matter-free basis, not ash-free basis, by appropriate means to be mentioned later.

CLASSIFICATION BY PROXIMATE ANALYSIS

The proximate analysis of coal consists in the determination by prescribed methods⁹⁵ of moisture, volatile matter, ash, and fixed carbon by difference. Volatile matter consists of the products other than "moisture" given off when the coal is heated according to the prescribed method; fixed carbon is the solid residue other than ash obtained in the same process of destructive distillation. Thus, on the dry, ash-free basis, volatile matter plus fixed carbon equals 100 per cent, and either of these complementary terms is satisfactory

for classification purposes. Also, either one of them is sufficient to determine the "fuel ratio," that is, the fixed carbon divided by the volatile matter, which is sometimes used instead.

Fixed carbon on the dry, ash-free basis has also been called "carbon ratio"⁹⁸ because it may be calculated from an analysis on the as-received basis by dividing the fixed carbon by the sum of volatile matter and fixed carbon.

Volatile Matter or Fixed Carbon, and Fuel Ratio. The use of volatile matter or fixed carbon (ashless coke residue) dates back to the earliest attempts at coal classification. Thus, Regnault⁹⁶ in 1837 reported fixed carbon as well as ultimate analysis and other characteristics, and Gruner,⁹⁸ who extended the system, included both volatile matter and fixed carbon. In 1911, Gruner and Bousquet,⁹⁹ still using the same system, indicated that the primary classification depended upon the proportion of volatile matter and the nature of coke, as shown in Table XIII.

Gruner and Bousquet relegated ultimate analyses to a secondary position for classification purposes as shown by Table XI.

Hilt⁹⁹ classified coals on the basis of parts of volatile matter per hundred parts of coke.

In the United States, the proximate analysis has nearly always been favored for classification purposes. Thus, Johnson,¹⁰⁰ in reporting on the evaporative power and other properties of United States and foreign coals to the Navy in 1844, included volatile matter, fixed car-

⁹⁸ Fuller, M. L., *Econ. Geol.*, **15**, 225-35 (1920).

⁹⁹ Hilt, C., *Dinglers Polytech. J.*, **205**, 424-34 (1873).

¹⁰⁰ Johnson, W. R., *Senate Document* 386, 28th Congress (1844), 607 pp.

TABLE XIII

CLASSIFICATION OF COALS, SUPPOSEDLY PURE AND ASH-FREE ⁶⁹

Class or Type of Coal	Proportion of Fixed Carbon per 100 of Pure Coal	Proportion of Volatile Matter per 100 of Pure Coal	Nature and Aspect of the Coke	True Calorific Power Calories	Indus- trial Calorific Power * Kilograms of Water
1. Houilles sèches à longue flamme	55-60	45-40	Powdery or slightly sintered	8,000-8,500	6.70-7.50
2. Houilles grasses à flamme (charbons à gaz)	60-68	40-32	Completely agglomerated and mostly fused	8,500-8,800	7.60-8.30
3. Houilles grasses proprement dites (charbons de forge)	68-74	32-26	Fused and more or less swollen	8,800-9,300	8.40-9.20
4. Houilles grasses à courte flamme	74-82	26-18	Compactly fused	9,300-9,600	9.20-10
5. Houilles maigres ou anthraciteuses	82-90	18-10	Slightly sintered, mostly powdery	9,200-9,500	9-9.50
6. Anthracites	90-92	10- 8	Powdery, to sandy	9,000-9,200	9

* Water at 0° vaporized at 112° per kilogram of pure coal.

bon, and the fuel ratio, which is the ratio of fixed to volatile combustible matter.

Rogers,⁸⁶ in 1858, divided coals into four principal groups on the basis of the volatile-matter content of the coal as received, including moisture and ash. Ultimate analysis, specific gravity, etc., also formed a part of the classification.

Frazer,¹⁰¹ in a paper originally presented in 1877, preferred Johnson's method of using the ratio of fixed carbon to volatile combustible matter, which Frazer called "fuel ratio," and proposed limits for Rogers' classes.

Campbell⁹¹ criticized this classification because it considered all coals of 5 or less fuel ratio to be bituminous and made no provision for lignite. He concluded that

the fuel ratio was valuable only for the higher-rank coals. Later,¹⁰² in a summary of the coal fields of the United States, he used different values of fuel ratios for classifying the ranks described by Rogers and combined them with other characteristics for distinguishing coals of lower rank.

As will be discussed later, modern refinements in determining volatile matter have appreciably altered the results compared with certain previous methods. In a high-rank coal, a small change in the percentage of volatile matter makes a relatively large change in the fuel ratio. Therefore a revision of fuel-ratio limits formerly proposed for classification purposes has been necessary.

Campbell,¹⁰³ in 1926, on the basis of

¹⁰¹ Frazer, P., Jr., *Trans. Am. Inst. Mining Met. Engrs.*, 6, 430-51 (1879); *Second Geol. Survey Penna., Rept. of Progress MM.* (1879), pp. 128-58.

¹⁰² Campbell, M. R., *U. S. Geol. Survey, Professional Paper 100a* (1917), 33 pp.

¹⁰³ Campbell, M. R., *Proc. 1st Intern. Conf. Bituminous Coal*, 1, 5-64 (1926).

recent analyses then available, proposed the following limits:

KINDS OF COAL	FUEL RATIO (FIXED CARBON TO VOLATILE MATTER)
Anthracite	50-10
Semianthracite	10- 5
Semibituminous	5- 2.5
Bituminous	2.5-

In this and other papers of about the same date,^{104, 105} Campbell discussed burning characteristics and physical properties of the higher-rank coals, as well as means other than fuel ratios for differentiating the lower-rank coals.

Ashley has proposed several classifications for American coals. A paper presented in 1919¹⁰⁶ discussed the ratio of fixed carbon to volatile matter plus moisture, also the ratio of fixed carbon to moisture as received. It included a large table summarizing information about coal textures and types; the heating value, proximate and ultimate analyses for coal reduced to 6 percent ash and 1 percent sulfur but with as-received moisture; also various ratios for representative American coals; and names coined from the type localities. Later,¹⁰⁷ he proposed classification on the basis of coals calculated to 7 percent ash and dried at 68° F and 15 millimeters of mercury absolute pressure.

A few years later, Ashley prepared a paper¹⁰⁸ on the practical classification of coals, in which the principal classification was according to the fixed-carbon content of the coal with as-received moisture, but ash-free. In the bituminous and subbitu-

minous classes, the fixed-carbon range of each class was 7 percent. Fuel ratios were shown. The class names were coined from the relative amounts of volatile matter and moisture. Other analytical data were included for representative coals of each rank and type. Classification according to grade (impurities) was included. In 1930, Ashley¹⁰⁹ revised this classification somewhat, using fixed carbon ranges of six percent for most classes.

Seyler⁷³ in his original article on coal classification stated that, regardless of the carbon content determined by ultimate analysis, coals may be classified according to volatile matter as follows:

VOLATILE MATTER

Up to 8%	Anthracitic and pseudoanthracitic
8-16%	Carbonaceous and pseudocarbonaceous
16-26%	Short-flame coals (mostly semibituminous or subbituminous)
26-32%	Normal bituminous coals
Over 32%	Long-flame coals

In later articles Seyler paid considerable attention to volatile matter and graphically showed how the lines of equal volatile matter crossed his classification chart diagonally. He also pointed out⁴⁰ that it is possible to predict the approximate ultimate analysis of bright coals from the volatile matter alone, and he showed the amount of "displacement" of volatile matter in durain (splint) and fusain as compared with bright layers of the same coal. Fisher³⁹ also discussed the relation between coal constituents and volatile matter, and the correlation of the volatile matter with the carbon-to-hydrogen ratio.

Parr¹¹⁰ in 1906 proposed a system of

¹⁰⁴ Campbell, M. R., and others, *Virginia Geol. Survey, Bull.* 25, 116 (1925).

¹⁰⁵ Campbell, M. R., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 489-504 (1930).

¹⁰⁶ Ashley, G. H., *ibid.*, 63, 782-96 (1920).

¹⁰⁷ Ashley, G. H., *Coal Age*, 25, 167-71 (1924).

¹⁰⁸ Ashley, G. H., *Penna. Topographic Geol. Survey, Bull.* 89 (1926), 16 pp.

¹⁰⁹ Ashley, G. H., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 512-6 (1930).

¹¹⁰ Parr, S. W., *J. Am. Chem. Soc.*, 28, 1425-32 (1906)

classification based on the ratio of carbon in the volatile matter to total carbon. Dowling¹¹¹ in order to avoid the necessity of an ultimate analysis, suggested use of the split volatile ratio, which assumes that half of the volatile matter is combustible and may be classed with the fixed carbon, while the other half is inert and should be classed with the moisture. The formula therefore is:

$$\frac{\text{Fixed carbon} + 0.5 \text{ Volatile matter}}{\text{Moisture} + 0.5 \text{ Volatile matter}}$$

It was said that the quotients from this ratio are almost as satisfactory as the carbon-to-hydrogen ratio. However, it has already been pointed out that there is a close parallelism between the simple volatile-matter percentage and the carbon-to-hydrogen ratio. The split volatile ratio was used in part in the classification of the coals of the world¹¹² and also in a later work by Dowling¹¹³ on the coal resources of Canada.

Spooner¹¹⁴ has stated that the yields of various constituents in the volatile matter are more closely related to rank than has hitherto been suspected. The carbon oxides and water were found to be directly proportional, and the free hydrogen inversely proportional, to the oxygen content of the coal, and the remaining volatile constituents were directly proportional to the hydrogen content of the coal. Blacher¹¹⁵ has graphed the volatile matter of

fuels versus the calculated percentage of hydrocarbons in the volatile matter, for classification purposes.

A great many investigators have studied the effect of temperature on the yield and composition of volatile products obtained from coals of various ranks and types. Florentin¹¹⁶ differentiated hard anthracites, true Welsh anthracites, and semi-anthracites, by means of the volume of total gas given off to 700° C by 1 gram of ash-free coal. He used this "characteristic gas volume" to supplement usual tests such as the percentage of volatile matter and the density.

Ramzin¹¹⁷ proposed the classification of coals from European Russia according to volatile matter on a dry, ash-free basis and to the nature of the coke resulting from the crucible test.

Meurice,¹¹⁸ in discussing the coking capacity of coals, cited the volatile-matter limits used by about a dozen European authorities in classifying various coals.

Graphic Studies of Proximate Analyses. Parr¹¹⁹ presented the proximate and ultimate analyses of coals in circular diagrams or "pie charts," which showed the various constituents and separated volatile matter into combustible and inert fractions.

Grout⁸⁷ presented the entire proximate analysis of coals on the triaxial diagrams which he used for graphing ultimate analyses. This was accomplished by locating the point representing ultimate analysis by means of a small equilateral triangle whose area represented the percentage of fixed carbon. The percentages of volatile matter, moisture, and ash were represented by the areas of smaller triangles formed in

¹¹¹ Dowling, D. B., *Can. Mining J.*, **29**, 143-6 (1908); *Can. Dept. Mines, Geol. Survey, Rept.* **1035**, 43-5 (1909).

¹¹² McInnes, W., Dowling, D. B., and Leach, W. W., Editors, 12th Intern. Geol. Congress, *The Coal Resources of the World*, Morang & Co., Ltd., Toronto, Canada, 1913, Vol. 1, civ + 371 pp.

¹¹³ Dowling, D. B., *Can. Dept. Mines, Geol. Survey, Memoir* **59** (1915), 157 pp.

¹¹⁴ Spooner, C. E., *J. Inst. Fuel*, **11**, 134-40 (1937).

¹¹⁵ Blacher, C., *Feuerungstechn.*, **13**, 69-70, 84-6, 95-8, 126-7, 148-52 (1925).

¹¹⁶ Florentin, D., *Ann. fals.*, **25**, 453-9 (1932).

¹¹⁷ Ramzin, L. K., *Bull. Inst. Fuel Research (Russia)*, No. 1, pp. 97-103, 1924.

¹¹⁸ Meurice, A. A., *Colliery Guardian*, **117**, 1559-60 (1919).

extensions of the sides of the fixed-carbon triangle.

Fisher¹¹⁹ has graphed proximate analyses on a triaxial diagram in which volatile matter, fixed carbon, and moisture total 100 percent. Wong¹²⁰ has plotted proximate analyses on a triaxial graph. Wang¹²¹ has similarly graphed the analyses of Chinese coals and has also plotted moisture, fixed carbon, and volatile matter against fixed carbon. Separate curves were shown for Paleozoic and Mesozoic coals.

Rose¹²² has shown how to correlate graphically proximate and ultimate analyses on any purity basis by means of "multibasic coal charts," which will be described later.

Availability of Good Proximate Analyses. Inexpensive proximate analyses—moisture, volatile matter, fixed carbon, and ash—are almost universally available for commercial coals.

It has long been known that the yield of volatile matter and fixed carbon obtainable from a particular sample of coal depends upon the temperature to which the coal is heated, the rate and duration of heating, and other factors. The results are also subject to errors resulting from oxidation, mechanical losses due to "sparking" of noncoking fuels, etc. As a result, volatile-matter determinations made under various conditions will give somewhat different results.

Fieldner¹²³ has reviewed American standard methods of coal analysis from 1899 to 1929 with reference to classifica-

tion problems. Lowry and Junge⁹⁸ concluded that the "reasonable" permissible difference for the same analyst making duplicate determinations of volatile matter on the same sample of coal is 0.5 percent for both bituminous coal and anthracite. Radmacher¹²⁴ has tabulated the complete details of fifteen different volatile-matter methods used in America, Austria, Belgium, Denmark, England, France, Germany, Holland, and Poland. It is not within the scope of this chapter to cite the many papers which present comparative volatile-matter results obtained under various conditions. It is sufficient to say that, when volatile matter is determined under appropriate standardized conditions, the results are reproducible with sufficient accuracy for classification purposes.

CLASSIFICATIONS INVOLVING BOTH PROXIMATE ANALYSIS AND CALORIFIC VALUE

Many of the classifications already described include heating value in a supplementary way. Since most coal is burned to produce heat, calorific value is obviously of great importance, and the following discussion relates to systems in which calorific value forms an essential part of the classification.

When lignites, subbituminous coals, and low-rank bituminous coals of similar petrographic composition are compared on the moist, ash-free basis, it is found that there is a close relation between rank and heating value, but their volatile matter or fixed carbon does not correlate closely with rank. On the other hand, the calorific value of high-rank bituminous and anthracitic coals does not form a sufficient basis for classification, but such coals can be readily classified according to volatile matter or fixed carbon.

¹¹⁹ Fisher, D. J., *J. Geol.*, **35**, 639-46 (1927).
¹²⁰ Wong, W. H., *Bull. Geol. Soc. China*, **6**, 65-7 (1927).

¹²¹ Wang, H. S., *ibid.*, **7**, 175-83 (1928); *Fuel*, **8**, 244-8 (1929).

¹²² Rose, H. J., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 541-53 (1930).

¹²³ Fieldner, A. C., *ibid.*, **88**, 585-96 (1930).

¹²⁴ Radmacher, W., *Brennstoff-Chem.*, **19**, 217-26, 237-43 (1938); *Fuel*, **18**, 228-46 (1939).

Therefore a combination of proximate analysis and calorific value has been found very practical for classifying the entire range of coals. These factors have been combined in a variety of ways. For example, Parr¹¹⁰ first proposed a classification which took into account volatile carbon, total carbon, inert volatile matter, and the "gross coal index," which was the sum of carbon, "available hydrogen," and sulfur. These last three constituents were considered to represent the actual fuel present, and their sum would be found to correlate approximately with calorific value. Later, Parr^{81, 125} proposed a system of classification based on the calorific value and volatile matter of "unit coal," which is coal calculated to the dry, mineral-matter-free basis by a special formula. Parr presented the classification in the form of a graph showing boundary lines which had been arbitrarily selected to separate the various ranks of coal. The later reference¹²⁵ recommends different boundary lines from the original publication.

The Parr classification has not been much used in the form in which it was presented, but the simplicity and advantages of the general method were at once apparent, and it has had much influence on subsequent classification developments.

Stansfield,¹²⁶ in 1925, studied the classification of Alberta coals of all ranks from lignite to low-volatile bituminous, according to Parr's proposal. He concluded that a satisfactory classification of the low-rank coals was impossible on the dry basis, and instead used volatile matter and calorific value on the basis of coal with moisture as mined, but with ash adjusted to 10 per-

cent. Several years later, additional data were presented by Stansfield and Sutherland,¹²⁷ in which the analyses were graphed on the "pure raw coal" basis, that is, coal with moisture as mined but calculated free of mineral matter. For comparison, a graph of the same analyses on the Parr "unit coal" basis was included.

Thom¹²⁸ also stressed the importance of moisture in the classification of low-rank coals and modified Parr's proposal by graphing volatile matter plus moisture versus calorific value, using ash-free analyses on the air-dry basis.

Landsberg¹²⁹ described methods used by the German State Railways to classify coals, one of which consisted in plotting the calorific value of clean coal against its volatile-matter yield.

Li and Loh¹³⁰ concluded that Parr's method was applicable to at least a great majority of Chinese coals.

Ralston⁸² in 1915 graphically correlated ultimate analyses with volatile matter and calorific values. Seyler⁷⁹ illustrated the superimposing of the Parr classification on his carbon-hydrogen diagram. Rose¹²² showed the correlation of American fuels from peat to anthracite by the Parr, Seyler, and other classifications, on his "multi-basic coal chart."

Calorific Value of Volatile Matter. In the gas industry, use has long been made of formulas which connect proximate analysis with calorific value in various ways. Fixed carbon is assumed to have a constant calorific value per unit, and the difference between the total calorific value of

¹²⁷ Stansfield, E., and Sutherland, J. W., *Can. Mining Met., Bull.* **210**, 1158-86 (1929).

¹²⁸ Thom, W. T., Jr., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 282-8 (1925), **88**, 406-8 (1930).

¹²⁹ Landsberg, F., *Glückauf*, **61**, 1427-39 (1925).

¹³⁰ Li, S. H., and Loh, H. T., *Eng. Quart., Univ. Chekiang*, **2**, 14-46 (1937).

¹²⁵ Parr, S. W., *Univ. Illinois, Eng. Exp. Sta., Bull.* **180** (1928), 59 pp.; *Fuel*, **16**, 52-8, 72-85 (1937).

¹²⁶ Stansfield, E., *Trans. Can. Inst. Mining Met.*, **28**, 252-66 (1925).

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a coal and that remaining in the fixed carbon gives the number of heat units in the volatile matter, i.e., the gas and tar. Dividing this figure by the percentage of volatile matter is assumed to give a figure which indicates the quality of the gas.

Salvadori and Mondini¹³¹ in classifying lignites recommended the use of "factor α ," which represented the amount of heat in each 1 percent of volatile matter obtainable at 500° C from the lignite, assuming that the fixed carbon obtained under the specified conditions had a heating value of 8,100 calories per gram. Landsberg¹²⁹ described the classification of German railway fuel by plotting the percentage of volatile matter against the calorific value per 1 percent of volatile matter.

De Goey and Brender-à-Brandis¹³² used the term "specific value number," or the letter omega to designate the number of calories in the gas per 1 percent of volatile constituents in the coal by the Geipert method. This value was highest for anthracite and decreased through bituminous coals to a low value for cellulose.

Burrough, Swartzman, and Strong¹³³ used the term "specific volatile index" to designate the following ratio, using analyses obtained by standard American methods:

S.V.I. =

$$\frac{\left. \begin{array}{l} \text{Determined Btu in coal} \\ - (14,500 \times \text{Weight of fixed carbon}) \end{array} \right\}}{\text{Percent of volatile matter}}$$

These authors studied the application of this index to Canadian fuels of all ranks, and they concluded that it places coals in

increasing value from peats to anthracites, according to their rank. For graphic presentation, the index was plotted against volatile matter percentage.

These authors showed a set of limits calculated on the dry, ash-free basis, for the classification of coals for use in the byproduct coking industry, and another set of limits was shown in a chart of specific volatile indices on the "unit coal" basis, arranged for correlation with the Parr and Seyler systems of classification.

Calculation of Calorific Value from Proximate and Ultimate Analysis. With modern bomb-calorimeter equipment, the calorific value of coal is determined rapidly, inexpensively, and precisely; in fact, this should be one of the most accurate determinations made on coal. Lowry and Junge⁹⁶ concluded that a reasonable permissible difference for duplicate determinations by the same laboratory was 0.5 percent, and for the most precise laboratory, 0.2 percent. However, bomb calorimeters were formerly less satisfactory and less widely available, so that many methods have been proposed for calculating calorific values from proximate or ultimate analyses. (See Chapter 4.)

AMERICAN STANDARD SPECIFICATIONS FOR CLASSIFICATION OF COALS BY RANK

The most extensive project ever undertaken on the classification of coals was begun in the United States in 1927 and was carried on actively for some ten years, about sixty specialists from the United States and Canada cooperating. This work, which was sponsored by the American Standards Association and the American Society for Testing Materials, led to the preparation and adoption of the present American Standard Specifications for Classification of Coals by Rank D388-

¹³¹ Salvadori, R., and Mondini, F., *Ann. chim. applicata*, **11**, 108-13 (1919).

¹³² De Goey, H. J. A., and Brender-à-Brandis, G. A., *Gas- u. Wasserfach*, **72**, 1237-42 (1929).

¹³³ Burrough, E. J., Swartzman, E., and Strong, R. A., *Can. Dept. Mines, Mines Branch, Invest. Fuels Fuel Testing 1930, 1931*, **725**, 36-50 (1933).

38¹³⁴ and by Grade D389-37,¹³⁵ Standard Definitions for Commercial Varieties of Bituminous and Subbituminous Coals D493-39,³¹ and Standard Method for Designating the Size of Coal from Its Screen Analysis D431-38.¹³⁶

Furthermore, it led to the critical study and improvement of various testing methods incidental to classification, and to the preparation of a large number of technical papers relating to improved testing methods and coal classification. It also resulted in the resampling of various coal areas where the reliability of previous coal analyses were questioned.

Fieldner¹³⁷ and Rose¹³⁸ have described the organization of the committees, the viewpoints, and the progress of this undertaking.

A.S.T.M. Classification by Rank. The resulting classification is summarized in Table XIV, but reference should be made to the complete standard¹³⁴ for details of classification, sampling, special test methods, and calculation of results. Both the Parr formulas and an approximation formula are given for calculating analyses to the mineral-matter-free basis.

These specifications, published in tentative form in 1934, were adopted as standard in 1937, with slight revisions in 1938, since when there has been no request for further revision.

¹³⁴ *Am. Soc. Testing Materials, Standards*, Pt. III, p. 1, 1939.

¹³⁵ *Am. Soc. Testing Materials, Standards*, Pt. III, p. 7, 1939.

¹³⁶ *Am. Soc. Testing Materials, Standards*, Pt. III, p. 49, 1939.

¹³⁷ Fieldner, A. C., *Proc. 2nd Intern. Conf. Bituminous Coal*, 1, 632-50 (1928); *U. S. Bur. Mines, Circ. 6094* (1929), 13 pp.; *Fuel*, 8, 473-81 (1929); *Ind. Standardization*, 7, 273-1 (1936).

¹³⁸ Rose, H. J., *Proc. 3rd Intern. Conf. Bituminous Coal*, 2, 839-49 (1931); *Ind. Eng. Chem.*, 26, 140-3 (1934).

Hendricks,¹³⁹ in summarizing this method of classification, stated:

The designation of any individual coal in this standard system would differ in only a few borderline cases from the designation by fuel ratios that has long been used by the Geological Survey and the Bureau of Mines, U. S. Department of the Interior. Such differences as do exist are the result of scientifically sound refinements of the earlier system.

Freeman¹⁴⁰ has proposed a convenient diagrammatic representation of this classification, as shown in Fig. 5.

The latest U. S. Geological Survey map of the coal fields of the United States¹⁴¹ shows the geographical limits of occurrence of the four major classes of Table XIV, with low-volatile bituminous coal areas shown separately from areas of other bituminous coals.

For a graphic study of United States coals according to the A.S.T.M. standard specifications by rank, reference should be made to Fieldner, Selvig, and Frederic,¹⁴² who graphed 316 typical coals of all ranks from the various coal fields of the United States. Figure 1 of reference 142 shows the arrangement of the entire series when graphed according to dry fixed carbon and moist Btu, both on the mineral-matter-free basis. Figures 2, 3 and 4 of reference 142 show enlarged sections of the diagram, with the individual points identified as to source and caking properties.

Selvig, Ode, and Fieldner¹⁴³ have dis-

¹³⁹ Hendricks, T. A., *Econ. Geol.*, 33, 136-42 (1938).

¹⁴⁰ Freeman, B. C., *ibid.*, 33, 570-1 (1938).

¹⁴¹ Averitt, P., *U. S. Geol. Surv.*, 2-pt. map, "Coal Fields of the United States," 56 by 85 inches, 1942.

¹⁴² Fieldner, A. C., Selvig, W. A., and Frederic, W. H., *U. S. Bur. Mines, Rept. Investigations* 3296R (1939), 22 pp.

¹⁴³ Selvig, W. A., Ode, W. H., and Fieldner, A. C., *Trans. Am. Inst. Mining Met. Engrs.*, 108, 188-96 (1934).

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TABLE XIV

A.S.T.M. CLASSIFICATION BY RANK *

Legend: F.C. = fixed carbon; V.M. = Volatile matter; Btu = British thermal units.

Class	Group	Limits of Fixed Carbon or Btu Mineral-Matter-Free Basis	Requisite Physical Properties
I. Anthracitic	1. Meta-anthracite	Dry F.C., 98 percent or more (dry V.M., 2 percent or less)	Nonagglomerating †
	2. Anthracite	Dry F.C., 92 percent or more and less than 98 percent (dry V.M., 8 percent or less and more than 2 percent)	
	3. Semianthracite	Dry F.C., 86 percent or more and less than 92 percent (dry V.M., 14 percent or less and more than 8 percent)	
II. Bituminous §	1. Low-volatile bituminous coal	Dry F.C., 78 percent or more and less than 86 percent (dry V.M., 22 percent or less and more than 14 percent)	Either agglomerating or nonweathering ¶
	2. Medium-volatile bituminous coal	Dry F.C., 69 percent or more and less than 78 percent (dry V.M., 31 percent or less and more than 22 percent)	
	3. High-volatile A bituminous coal	Dry F.C., less than 69 percent (dry V.M., more than 31 percent); and moist ‡ Btu, 14,000 or more	
	4. High-volatile B bituminous coal	Moist ‡ Btu, 13,000 or more and less than 14,000	
	5. High-volatile C bituminous coal	Moist Btu, 11,000 or more and less than 13,000	
III. Subbituminous	1. Subbituminous A coal	Moist Btu, 11,000 or more and less than 13,000	Both weathering and nonagglomerating
	2. Subbituminous B coal	Moist Btu, 9,500 or more and less than 11,000	
	3. Subbituminous C coal	Moist Btu, 8,300 or more and less than 9,500	
IV. Lignite	1. Lignite	Moist Btu, less than 8,300	Consolidated Unconsolidated
	2. Brown coal	Moist Btu, less than 8,300	

* This classification does not include a few coals which have unusual physical and chemical properties and which come within the limits of fixed carbon or Btu of the high-volatile bituminous and subbituminous ranks. All these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free Btu.

† If agglomerating, classify in low-volatile group of the bituminous class.

‡ Moist Btu refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

§ It is recognized that there may be noncaking varieties in each group of the bituminous class.

|| Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of Btu.

¶ There are three varieties of coal in the high-volatile C bituminous coal group, namely, Variety 1, agglomerating and nonweathering; Variety 2, agglomerating and weathering; Variety 3, nonagglomerating and nonweathering.

cussed the boundary lines and reasons for classifying high-rank coals by fixed carbon, or volatile matter, on the dry basis, and low-rank coals by Btu on the moist basis. There is ample justification for this; in fact, a long and systematic study of the

coals. However, this procedure seems to be sound, desirable, and actually necessary from practical classification standpoints.

For the purpose of simple and practical classification of coals according to rank, the present standard specifications appear to

Anthracitic		Bituminous				Subbituminous		Lignitic	
Nonweathering					Weathering	Nonweathering	Weathering		
98 92 86 78 69 F.C. (Dry Basis)									
2	11	Antra-cite 12	I ₁ = Meta Anthracite						
8		Semi-Anthra-cite 13							
14			Low Volatile Bituminous II ₁					Consolidated	Unconsolidated
22				Medium Volatile Bituminous II ₂					
31									
					High Volatile A Bituminous II ₃				Over 14000
					High Volatile B Bituminous II ₄				14000
					High Volatile C Bituminous II ₅			Subbituminous A III ₁	13000
					Variety 1	Variety 2	Variety 3		11000
								Subbituminous B III ₂	9500
								Subbituminous C III ₃	8300
								Lignite IV ₁	Brown Coal IV ₂
									Under 8300
Nonagglomerating		Agglomerating				Nonagglomerating			

g. 5. Diagram of A.S.T.M. Classification of Coals by Rank (Freeman ¹⁴⁰).

properties of the coals of the United States and Canada, representing about two-thirds of the world's known coal reserves, led to practically unanimous agreement by the committees studying the subject. As would be expected, the reasons for changing from fixed-carbon to Btu limits and from the dry to the moist basis when classifying high- and low-rank coals are not apparent to everyone, particularly to those who have had little familiarity with low-rank

be about as satisfactory ones as can be developed without adding refinements which would complicate their use for ordinary technical purposes. Although either fixed carbon or Btu alone may be sufficient to determine the class and group in which a coal belongs, both items should be stated when describing a coal. Condensed symbols for this purpose are provided for in the specifications.

For specialized requirements, the

A.S.T.M. classification may be supplemented by various chemical or physical tests referred to elsewhere in this chapter. A knowledge of the petrographic composition—classification by type—is often desirable, but unfortunately there is not at present any simple and widely accepted method for quantitatively determining the proportion of various petrographic constituents in shipments of coal. The agglomerating and weathering characteristics specified as requisite physical properties in certain borderline cases of the A.S.T.M. classification recognize to some extent the practical importance of differences in type of constituents as well as rank. The first footnote of Table XIV excludes a few coals which have unusual properties because of differences in petrographic constituents.

Canadian Participation. Throughout the committee work which led to the adoption of the several A.S.T.M. specifications relating to the classification of coal, Canadian members made important contributions to the researches and deliberations. In 1928, the National Research Council of Canada appointed the Associate Committee on Coal Classification and Analysis to parallel the American group and to study the application of various proposals to Canadian coals.

Canadian representatives had a prominent part in the formulation of the A.S.T.M. specifications for classification by rank and by grade, and these were unanimously accepted by the associate committee, with recommendation for their general use in Canada. This subject is covered by an official report which discusses the A.S.T.M. classifications and their application to Canadian coals.¹⁴⁴ The report contains a chart illustrating the application of the rank classification to coals from the various Canadian fields, with coal areas and

caking properties identified. The effect of the A.S.T.M. classification on Canadian coal statistics and customs tariff is discussed.

Use of Agglomerating Properties for Classification. According to the standard specifications¹³⁴ referred to in the preceding section, a coal cannot be classed as semianthracite unless it is nonagglomerating. In the classification of coals near the borderline of the bituminous and subbituminous classes, a knowledge of agglomerating properties is usually necessary. The specifications state:

Pending the adoption of a method by the American Society for Testing Materials, the coke-button grading test¹⁴⁵ afforded by the examination of the residue in the platinum crucible incident to the volatile matter determination shall be used.

If the carbonized residue from heating 1 gram of coal in the standard volatile-matter test can be poured out of the crucible as a powder, or if it cannot support a 500-gram weight without being pulverized, the coal is classed as nonagglomerating. If, however, the coal produces a coherent residue which will support a 500-gram weight, or a button showing swelling or coke structure, it is considered to be agglomerating. The properties of the carbonized residue from the volatile-matter test has been utilized since the earliest attempts at coal classification. Further reference to caking, coking, and agglutinating properties will be made later in this chapter.

Use of Weathering or Slacking Properties. Information on weathering or slacking properties is often necessary for the classification of coals near the boundary between the bituminous and subbituminous classes. Weathering refers to the tendency of low-rank coals to break apart when they

¹⁴⁴ Anon., *Nat. Research Council Can., Rept.* 814 (1939), 26 pp.

¹⁴⁵ Gilmore, R. E., Connell, G. P., and Nicolls, J. H. H., *Trans. Am. Inst. Mining Met Engrs.*, 108, 255-65 (1934).

dry out, the breakage being increased by repeated wetting and drying, as by exposure to weather.

The A.S.T.M. specifications¹³⁴ state that, pending the adoption of an A.S.T.M. method, the weathering or slacking characteristics of coals shall be determined by the U. S. Bureau of Mines method,¹⁴⁶ modified by using a standard humidity of 30 to 35 percent. The method consists in air-drying lumps of coal 1 to 1.5 inches in size, immersing them in water, and again air-drying. The percentage of coal which then passes through a 0.263 square mesh screen, after deducting a blank sieving test, is the weathering or slacking index of the coal. If this amounts to more than 5 percent, the coal is considered to be weathering from the standpoint of classification.

Stansfield, Lang, and Gilbert¹⁴⁷ have investigated the effect of oven humidity on accelerated weathering tests of coal. Campbell,¹⁴⁸ in 1908, recommended weathering behavior as a criterion for differentiating between bituminous and subbituminous coal, the latter term having just been adopted for use in U. S. Geological Survey publications. He described and illustrated differences in the breakage by weathering of subbituminous coal and lignite.¹⁰² Parr and Mitchell¹⁴⁹ discussed the slacking of bituminous coal and its interpretation, including the effect of bands of mineral charcoal, fusain. Seawright¹⁵⁰ has investigated the slacking properties of South

Dakota coals, and Yancey, Johnson, and Selvig^{151, 152} have reported the slacking characteristics, agglutinating values, friability, etc., of about 100 coals from Washington and other states. Ramzin¹⁵³ has qualitatively described the weathering characteristics of coals from various Russian fields.

Moisture and Coal Classification. The A.S.T.M. standard specifications for the classification of coals by rank¹³⁴ provides for the classification of lignitic, subbituminous, and high-volatile bituminous coals on the moist basis. When the coals contain visible moisture as sampled, they are brought to a standard condition of moisture equilibrium at 30° C over a saturated solution of potassium sulfate, an atmosphere of 97 percent humidity, as suggested by Stansfield and Gilbert.¹⁵⁴

Rees, Reed, and Land¹⁵⁵ have studied equilibration methods for determining moisture in Illinois coals for classification by rank. From various investigations of the general subject, it appears likely that some modification of the present A.S.T.M. provisions relating to moisture equilibration may prove desirable.

Hicks¹⁵⁶ has studied the moisture sorption of South Wales anthracite in an atmosphere of 90 percent relative humidity, to determine whether this would provide a more accurate basis for classification than the ultimate analysis. This hope was not fulfilled, but a fairly good relation was

¹⁴⁶ Fieldner, A. C., Selvig, W. A., and Frederic, W. H., *U. S. Bur. Mines, Rept. Investigations* 3055 (1930), 24 pp.

¹⁴⁷ Stansfield, E., Lang, W. A., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, 108, 243-53 (1934).

¹⁴⁸ Campbell, M. R., *Econ. Geol.*, 3, 134-42 (1908).

¹⁴⁹ Parr, S. W., and Mitchell, D. R., *Ind. Eng. Chem.*, 22, 1211-2 (1930).

¹⁵⁰ Seawright, W. V., *S. Dakota Geol. Natural Hist. Surv., Rept. Investigations* 12 (1932), 14 pp.

¹⁵¹ Yancey, H. F., Johnson, K. A., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper* 512 (1932), 94 pp.

¹⁵² Yancey, H. F., and Johnson, K. A., *Trans. Am. Inst. Mining Met. Engrs.*, 101, 171-96 (1932).

¹⁵³ Ramzin, L. K., *Proc. 2nd Intern. Conf. Bituminous Coal*, 1, 925-35 (1928).

¹⁵⁴ Stansfield, E., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, 101, 125-43 (1932).

¹⁵⁵ Rees, O. W., Reed, F. H., and Land, G. W., *Illinois State Geol. Survey, Rept. Investigations* 58 (1933), 34 pp.

¹⁵⁶ Hicks, D., *Fuel*, 20, 106-17 (1941).

found between moisture sorption and carbon and hydrogen contents of the anthracite.

The general subject of moisture in coal is covered by a separate chapter, and only a few further references can be justified at this point. Ashley,^{106, 109} Campbell,^{102, 105} Stansfield,^{126, 154} and Thom¹²⁸ have emphasized the desirability of classifying low-rank coals on the moist basis.

Collier,¹⁵⁷ in 1903, used the ratio of moisture to fuel ratio for the classification of Alaskan lignites. Petrascheck¹⁵⁸ proposed the relative hygroscopicity of dry coal for the classification of brown coals. Kammerer and Guth¹⁵⁹ stated that the hygroscopic water content can be used for classifying various types of coal. Fisher¹¹⁹ and Wong¹²⁰ graphed proximate analyses on a triaxial diagram which emphasizes the moisture content of the low-rank coals. Wang¹²¹ has graphed moisture versus rank for forty Chinese coals.

CORRECTING COAL ANALYSES TO THE MINERAL-MATTER-FREE BASIS

The A.S.T.M. standard specifications for classification of coals by rank¹³⁴ require that analyses be calculated to the mineral-matter-free basis either by the Parr or approximation formulas given in the specifications. The purpose is to classify coals as nearly as possible on the basis of the pure coal substance, calculated free from variable and accidental mineral impurities.

Ash-Free Basis. More than a hundred years ago, Regnault⁶⁶ calculated analyses to the ash-free basis for classification purposes, and it has been customary ever since to use some method of reducing the effect

of impurities on coal analyses. A common method has been to calculate the analytical results to an ash-free basis, but this introduces substantial errors because the weight of ash obtained by ignition to constant weight is not the same as the weight of mineral impurities present in the original coal. This is due principally to expulsion of water of hydration from the shaly impurities, the conversion of iron-pyrites to iron oxide, and the expulsion of more or less carbon dioxide from carbonates. The total error resulting from these causes is usually too large to be ignored, and various procedures have been proposed for minimizing the errors.

Use of Ratios. The use of ratios such as the "fuel ratio," fixed carbon to volatile matter, or the carbon-to-hydrogen ratio, avoids the step of calculating analyses to an ash-free basis. However, it does not correct for certain errors due to mineral impurities. For example, the water of hydration which is evolved when shaly impurities are heated affects the volatile matter and hydrogen percentages, while carbonates may contribute carbon dioxide which affects volatile matter and carbon percentages. Fixed carbon, which is obtained by difference, is affected by errors of both the volatile matter and ash percentages.

Correction Formulas. The simplest way to minimize errors due to the presence of mineral impurities in coal is to use empirical formulas to correct the analytical results. Parr and Wheeler,¹⁶⁰ in 1909, proposed a formula for calculating the mineral matter in coal from the ash and sulfur percentages, which is still accepted as standard. Later papers by Parr^{81, 125} confirmed and amplified the formulas, which assume that the percentage of mineral matter in coal is

¹⁵⁷ Collier, A. J., *U. S. Geol. Surv., Bull.* **218** (1903), 71 pp.

¹⁵⁸ Petrascheck, W., *Braunkohle*, **25**, 761-4 (1926).

¹⁵⁹ Kammerer, V., and Guth, J., *Fuel*, **2**, 339-43 (1923).

¹⁶⁰ Parr, S. W., and Wheeler, W. F., *J. Ind. Eng. Chem.*, **1**, 636-42 (1909); *Univ. Illinois, Eng. Expt. Sta., Bull.* **37**, 1-67 (1909).

numerically equal to 1.08 ash plus 0.55 sulfur. The actual formulas used for calculating fixed carbon, volatile matter, and Btu to the mineral-matter-free basis are shown below. In the event of litigation, coal samples containing more than 1 percent carbon dioxide occurring as carbonates must be floated on a heavy liquid to reduce the amount to less than 1 percent. An alternative method involving sulfation of the ash of high-carbonate coals is also provided.

Except in case of litigation, the A.S.T.M. specifications permit the use of approximation formulas which are simpler to calculate and are of sufficient accuracy for most purposes. These approximation formulas were selected from a number proposed and tested by members of the classification committees.¹⁶¹ They are included in the following excerpt:¹⁶⁴

Calculation from "moist" basis:

Parr Formulas:

Dry, Mm-free F.C.

$$\frac{\text{F.C.} - 0.15S}{100 - (M + 1.08A + 0.55S)} \times 100$$

Dry, Mm-free V.M.

$$= 100 - \text{Dry, Mm-free F.C.}$$

Moist, Mm-free Btu

$$\frac{\text{Btu} - 50S}{100 - (1.08A + 0.55S)} \times 100$$

Note: The above formula for fixed carbon is derived from the Parr formula for volatile matter.

Approximation Formulas:

Dry, Mm-free F.C.

$$\frac{\text{F.C.}}{100 - (M + 1.1A + 0.1S)} \times 100$$

¹⁶¹ Fieldner, A. C., *Am. Soc. Testing Materials, Sectional Committee on Classification of Coals, General Circ. 42, Sub-Comm. II, Rept. 7* (1933).
¹⁶² Nicolls, J. H. H., *Can. Dept. Mines, Branch, Fuel Research Labs., Memo Regarding the Calculation of "Pure-Fuel" Calorific Values of Nova Scotia and New Brunswick Coals*, 1935, 14 pp. mimeo.

Dry, Mm-free V.M.

$$= 100 - \text{Dry, Mm-free F.C.}$$

Moist, Mm-free Btu

$$\frac{\text{Btu}}{100 - (1.1A + 0.1S)} \times 100$$

where Mm = mineral matter.

Btu = British thermal units.

F.C. = percentage of fixed carbon.

V.M. = percentage of volatile matter.

M = percentage of moisture.

A = percentage of ash.

S = percentage of sulfur.

Moist refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

G. Thiessen¹⁶² has compared the Parr and approximation formulas with values calculated from a consideration of the chemical analysis of the ash, for twenty-one coals. He also proposed¹⁶³ a modification of the Parr formula for calorific value, in which the constant for the sulfur correction varied with the rank of coal.

Barkley and Burdick¹⁶⁴ have presented a series of six charts for converting ordinary coal analyses on the moist or dry basis to the basis of results corrected by the Parr or approximation formulas. Cady and Rees¹⁶⁵ have discussed unit coal as a basis of standardization when applied to Illinois coals.

Drakeley and Hepburn¹⁶⁶ studied the effect of ash content on volatile matter by separating a coal into ten specific gravity fractions and determining volatile matter

¹⁶² Thiessen, G., *Illinois State Geol. Survey, Rept. Investigations 32*, 27-39 (1934); *Am. Inst. Mining Met. Engrs., Contrib. 68F* (1934), 12 pp.

¹⁶³ Thiessen, G., *Fuel*, **12**, 403-11 (1933); *Illinois State Geol. Survey, Rept. Investigations 32*, 7-25 (1934).

¹⁶⁴ Barkley, J. F., and Burdick, L. R., *U. S. Bur. Mines, Information Circ. 6933* (1937), 6 pp.

¹⁶⁵ Cady, G. H., and Rees, O. W., *Illinois State Geol. Survey, Rept. Investigations 32*, 41-55 (1934).

¹⁶⁶ Drakeley, T. J., and Hepburn, J. R. I., *J. Soc. Chem. Ind.*, **43**, 134-7T (1924).

on each. They concluded that this treatment produced a segregation of the petrographic constituents, so that such results do not permit a mathematical treatment of the problem. Formulas were presented for calculating the volatile matter of ash-free coal in the presence and absence of pyrites.

King, Maries, and Crossley¹⁶⁷ have systematically discussed the errors resulting from the presence of various mineral impurities in coal, and have proposed formulas including their corrections for carbon, hydrogen, volatile matter, and Btu determinations.

Seyler⁷⁹ recommended Parr's unit coal basis for classification, with a modification of the sulfur correction, and with the proviso that the hydrogen equivalent of water liberated from the shaly impurities should be deducted from the organic hydrogen.

Much of the published experimental evidence on correction formulas is based on a study of Btu determinations rather than on proximate and ultimate analyses. In 1898, Lord and Haas¹⁶⁸ recommended the *H* Btu, representing the ash-free, not mineral-matter-free, Btu corrected for the heating value of the sulfur in the coal. (*Note:* This should not be confused with another *H* value often used in recent years, which is simply Btu on the dry, ash-free basis.) The Parr formula for Btu has a correction factor for sulfur in the numerator. Drakeley¹⁶⁹ investigated the relation between calorific value and ash yields for certain English coals and concluded that an average factor of 1.125 was required to change the percentage of ash to mineral matter in the original coals. Purdon and Sapgirs¹⁷⁰

have reviewed various factors which have been proposed for changing the ash percentage to mineral matter.

Graphic Extrapolation. Brinsmaid,¹⁷¹ in 1909, proposed a graphic method for determining the Btu of pure coal. He hand-picked coal samples into low-ash and higher-ash portions, made various mixtures of these, and determined the Btu of each mixture. When graphed, the results fell close to a straight line, which was extrapolated to give the Btu at zero ash. Brinsmaid pointed out that errors in ultimate analysis occurred because of carbon dioxide and water derived from mineral impurities.

Stansfield,¹⁷² in 1925, adjusted analyses to a uniform 10 percent ash basis, in order to avoid too large corrections. This was done by interpolating on a curve of Btu versus ash, for float-and-sink fractions of coal. Stansfield and Sutherland^{127, 172} also used extrapolation to obtain Btu on a mineral-matter-free basis, and they have described their technique in some detail. Stansfield,¹⁷³ in 1931, graphically showed the variation of the individual items of proximate and ultimate analysis, as well as Btu, with the ash percentage of sink-and-float samples, for a single coal. Most of the results fell on straight lines.

Fieldner, Selvig, and Gibson¹⁷⁴ compared the corrected Btu values obtained by the Stansfield and Sutherland graphic extrapolation method with the results by the Parr, modified Parr, and ordinary dry, ash-free calculations, for seven coals. Close agreement was obtained by the graphic and Parr

¹⁷¹ Brinsmaid, W., *J. Ind. Eng. Chem.*, **1**, 65-8 (1909).

¹⁷² Stansfield, E., and Sutherland, J. W., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 614-26 (1930).

¹⁷³ Stansfield, E., *Proc. Fuel and Coal Symposium*, McGill Univ., Canada, 1931, 40 pp.

¹⁷⁴ Fieldner, A. C., Selvig, W. A., and Gibson, F. H., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 224-35 (1932); *Fuel*, **11**, 306-12 (1932).

¹⁶⁷ King, J. G., Maries, M. B., and Crossley, H. E., *J. Soc. Chem. Ind.*, **55**, 277-81T (1936).

¹⁶⁸ Lord, N. W., and Haas, F., *Trans. Am. Inst. Mining Met. Engrs.*, **27**, 259-71 (1898).

¹⁶⁹ Drakeley, T. J., *Trans. Inst. Mining Engrs. (London)*, **56**, 45-56 (1918).

¹⁷⁰ Purdon, A., and Sapgirs, S., *Fuel*, **12**, 40-6 (1933).

methods, using float-and-sink separations at 1.38 specific gravity. Hertzog¹⁷⁵ studied comparative Btu corrections obtained by seven different methods on float-and-sink fractions from Alabama coals. He recommended, as the most reliable method, use of the "pure coal constant" calculated from the Btu value and yield of the float-and-sink fractions at 1.35 specific gravity. This constant (the change in specific gravity for each 1 percent ash) is multiplied by the percentage of ash, and added to the determined Btu. This is the arithmetic equivalent of graphic extrapolation.

Thiessen and Reed¹⁷⁶ compared the graphic extrapolation method with the Parr unit coal formula for determining corrected Btu, and they concluded that the values corresponded closely. They found no advantage in the graphic method from the standpoint of accuracy, and it had the disadvantages of requiring more work and not being applicable to ordinary published analyses.

Both the graphic extrapolation method and much of the checking of correction formulas have been based on specific-gravity fractionation of coals. It has often been recognized that there was danger of segregation of both the coal and ash, and possible effect of heavy-gravity solutions on the coal, which would vitiate the results. However, it has been found empirically that, when Btu determinations are plotted against ash, the points nearly always fall close to a straight line, although some divergence has been reported both at the low- and high-specific-gravity ends. McCabe, Mitchell, and Cady¹⁷⁷ have reported on

this for certain Illinois coals and have emphasized the deviation from a straight line by graphing the Btu of unit coal versus specific gravity. They concluded that vitrain tended to concentrate in the light fractions, clarain in the intermediate, and mineral impurities, and to some extent fusain, in the heavy. Tideswell and Wheeler⁹⁷ have emphasized the advantages of purifying the coal by flotation or other mechanical means to remove as much as possible of the mineral impurities before analysis.

Acid Extraction of Impurities. Another method which has sometimes been used is to treat the coal with hot hydrofluoric and other acids to volatilize and extract the mineral impurities with minimum alteration of the coal substance. Fieldner, Selvig, and Taylor¹⁷⁸ have used this method for the determination of combustible matter in rocks. Turner¹⁸ in cooperation with the U. S. Bureau of Mines¹⁷⁹ investigated the effect of acid treatment on anthracite and bituminous coals. Under the conditions used, residual ash was 0.1 to 1.4 percent, but the loss of unit-coal Btu and carbon averaged about 2 percent and hydrogen about 0.1 percent. The indications were that a technique could be developed to reduce these losses. Karavaev and Rapoport¹⁸⁰ used cold hydrofluoric acid for 24 to 48 hours to minimize the risk of decomposing organic material.

GRAPHIC CORRELATION OF COAL CLASSIFICATION SYSTEMS

Reference has already been made to the close relation which exists between ultimate

¹⁷⁸ Fieldner, A. C., Selvig, W. A., and Taylor, G. B., *U. S. Bur. Mines, Tech. Paper 212* (1919), 22 pp.

¹⁷⁹ Fieldner, A. C., *Am. Soc. Testing Materials, Sectional Committee on Classification of Coal, Gen. Circ. 11, Sub-Comm. II, Rept. 2* (1929).

¹⁸⁰ Karavaev, N. M., and Rapoport, I. B., *Izvest. Teplotekh. Inst.*, **5**, 31-4 (1929).

¹⁷⁵ Hertzog, E. S., *Fuel*, **12**, 112-7 (1933).

¹⁷⁶ Thiessen, G., and Reed, F. H., *Illinois State Geol. Survey, Rept. Investigations 32*, 57-99 (1934); *Fuel*, **13**, 167-75, 208-17 (1934).

¹⁷⁷ McCabe, L. C., Mitchell, D. R., and Cady, G. H., *Illinois State Geol. Survey, Rept. Investigations 34*, p. 45-61 (1934).

and proximate analyses and calorific values of coals. The situation is complicated by the fact that more than ten different purity (moisture, ash, sulfur, nitrogen) bases have been proposed for comparing coal analyses for classification purposes.

Multibasic Coal Charts. Rose¹²² has devised a diagram called the "multibasic coal

analysis will fall in approximately the same area of the lower portion of the diagram as it will fall in the upper area when graphed according to fixed carbon and Btu.

This is illustrated by Fig. 7, which presents the analyses of forty samples of coal of all ranks, ranging from peat to anthracite, on the moist but ash-free basis. The

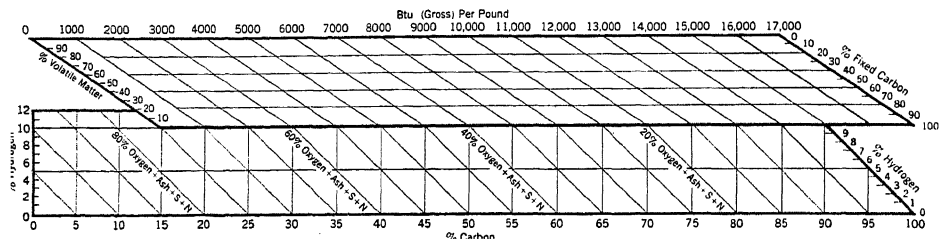


FIG. 6. Multibasic coal chart, showing method of construction.

chart" which permits convenient visual comparison of coal analyses graphed according to fixed carbon, volatile matter, Btu, or ultimate analyses, on any purity basis.

Figure 6 shows the general construction of the chart and provides enough information so that the whole chart, or any por-

tion of it, may be duplicated by drawing in the sloping lines on ordinary rectangular coordinate paper and adding the scales along the margins. To save vertical space, the upper and lower halves may be cut away and overlapped as in Figs. 7, 8, 9, and 10. The scales have been so selected that a coal graphed according to ultimate

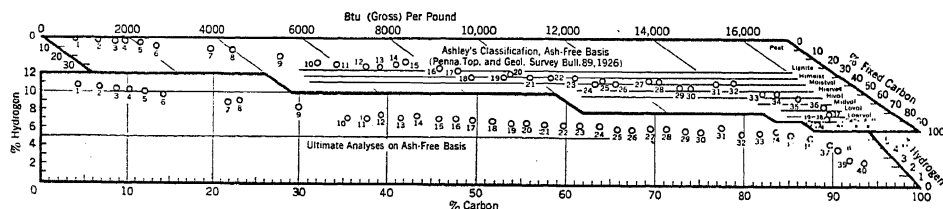


FIG. 7. Comparison of one of Ashley's classifications with ultimate analyses of same coals, on the multibasic coal chart.

tion of it, may be duplicated by drawing in the sloping lines on ordinary rectangular coordinate paper and adding the scales along the margins. To save vertical space, the upper and lower halves may be cut away and overlapped as in Figs. 7, 8, 9, and 10. The scales have been so selected that a coal graphed according to ultimate

The use of the multibasic coal chart for comparing various coal classifications is illustrated by Figs. 7, 8, and 9. The upper part of Fig. 7 shows the forty analyses divided according to one of Ashley's classifications,¹⁰⁸ which uses fixed carbon, mostly in 7 percent steps, to classify ash-free samples containing natural bed moisture.

Figure 8 presents the same analyses on the dry, ash-free basis. The upper area shows the division of high-rank coals by fuel ratios according to one of Campbell's proposals;¹⁰³ in the lower area the analyses after further recalculation to the sulfur-free basis have been divided into groups according to the ultimate-analysis limits of the Gruner classification.^{73, 181}

In Fig. 9 the analyses graphed in the lower area are likewise on the dry, ash-free, and sulfur-free basis and have been classified according to one of Seyler's proposals,¹⁸² which has analysis limits slightly different from those in Table XII of this chapter. In the upper area of Fig. 9 the analyses are on the same purity basis except that the special Parr corrections have been applied and the coals are graphed according to one of Parr's proposals.¹²⁵

These examples show the value of this method for visually comparing different systems of coal classification based on proximate analysis, ultimate analysis, or Btu.

Figure 10 illustrates the effect of recalculating a single coal analysis to various purity bases. In the upper area the points fall on a straight line originating in the 0 percent fixed carbon, 0 Btu corner. In the lower area, the points representing ultimate analyses move in a straight line away from the 0 percent carbon, 0 percent hydrogen corner when they are calculated free of ash, sulfur, or nitrogen, and they move in a straight line away from the point representing water when they are calculated free of moisture. When the Parr corrections are applied, the points deviate slightly from the straight-line relationship.

The multibasic coal chart appears to provide the most satisfactory graphic method

¹⁸¹ Gruner, E., and Bousquet, G., p. 16 of ref. 5.

¹⁸² Seyler, C. A., p. 80 of ref. 74.

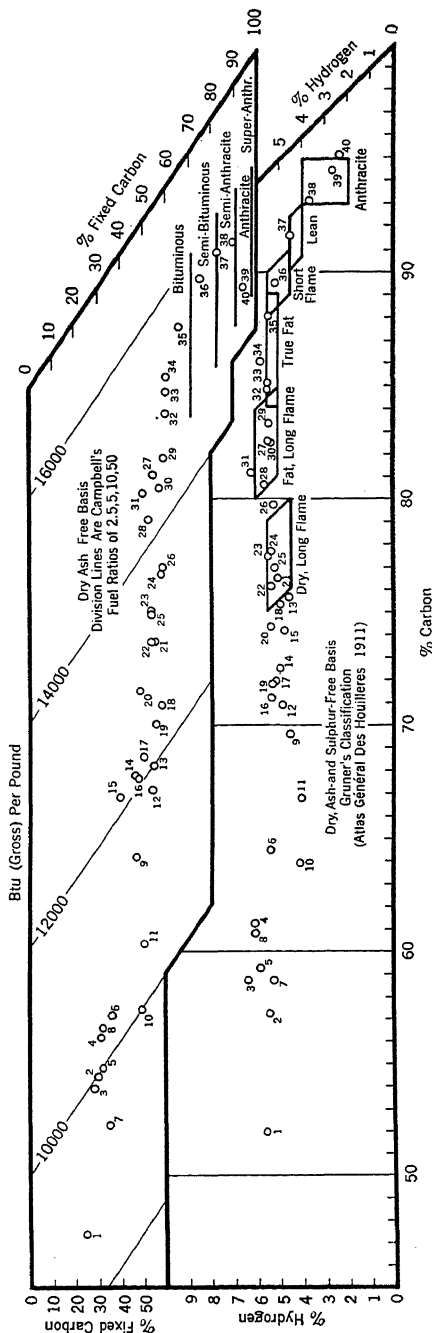


FIG. 8. Comparison of Campbell and Gruner classifications applied to the same coals, on the multibasic coal chart.

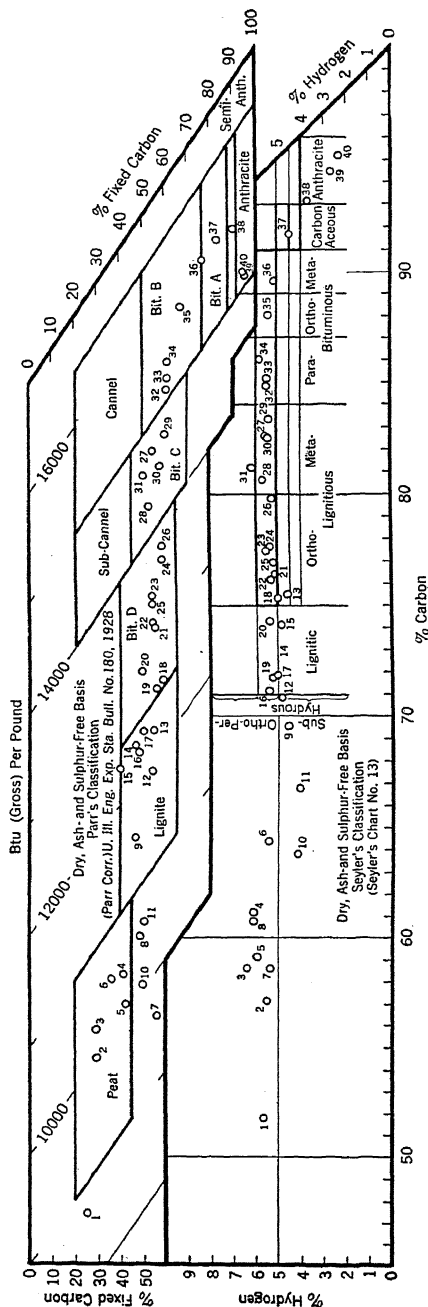


FIG. 9. Comparison of Parr and Seyler classifications applied to the same coals, on the multibasic coal chart.

for comparing coal classifications, and it is also frequently desirable for presenting coal analyses for other purposes. The scales in these charts necessarily represent a compromise since they must apply to coals of all ranks and purity bases and since, for convenience in drawing the charts on rectangular coordinate paper, the scales must be uniform and represent simple multiples of each other. Nevertheless, the correlation of the location of points in the two areas is surprisingly good when analyses covering a considerable range in values are graphed.

Other Graphic Correlations. Seyler¹⁸³ has graphically compared his classification with that of Gruner and also⁷⁹ with that of Parr. Rose⁵⁶ compared the Seyler and Gruner classifications.

CLASSIFICATION BY OTHER CHEMICAL AND PHYSICAL TESTS

In addition to the classifications by rank which have already been mentioned based on proximate and ultimate analysis and Btu, many other bases have been proposed. Since they have found only limited acceptance, and since the subject matter is covered in more detail by other chapters, only brief reference will be made to some of these proposals.

Extraction with Organic Solvents. Illingworth¹⁸⁴ attempted to correlate Seyler's classification according to ultimate analysis with the yields and characteristics of the pyridine extracts and residues from coking coals. The ulmin, alpha, beta, and gamma compounds were discussed in terms of the carbon-to-hydrogen ratio, coke yields, thermal stability, etc. Iki¹⁸⁵ investigated simi-

¹⁸³ Seyler, C. A., pp. 44-5 of ref. 74.

¹⁸⁴ Illingworth, S. R., *Fuel*, 1, 3-6, 17-9, 33-5, 49-51, 65-7, 89-90, 213-8 (1922); *Iron & Coal Trades Rev.*, 104, 575 (1922); *Gas World*, 90, Coking Section, 18-20 (1929).

¹⁸⁵ Iki, S., *Fuel*, 9, 412-20 (1930).

EXTRACTION WITH ALKALIES

lar characteristics of twenty-three Japanese coals.

Bone and his associates¹⁸⁶ have studied the extraction of coal with reference to its coking properties and rank, using samples ranging from brown coals and lignites to strongly coking bituminous coals.

Fischer, Broche, and Strauch¹⁸⁷ extracted coals of noncoking subbituminous to strongly coking semibituminous rank, with benzene under pressure at 285° C, and

Rose and Hill,¹⁸⁹ in a patent application filed in 1926, disclosed their discovery that coking coals could be almost completely dissolved at atmospheric pressure in hot anthracene oil and other related solvents, with subsequent recovery of the coal freed from insoluble mineral impurities, fusain, etc. The corresponding French patent¹⁹⁰ was issued in 1929 and was followed by European work on the general subject, e.g., by Gillet and Pirlot.¹⁹¹

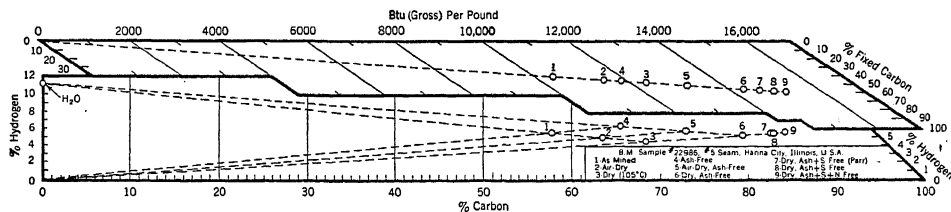


FIG. 10. Effect of calculating coal to various purity bases, on location of analysis on multi-basic coal chart.

attempted to correlate the properties of the residue and extract with the coking and swelling properties of the coals. Stadnikoff⁴⁸ distinguished between humic or common bituminous coals and boghead coals, partly by the fact that humic coals give a large yield of bitumen by extraction with organic solvents whereas boghead coals give a very small quantity, particularly if they are of the compact type. Laminated bogheads give a somewhat higher yield of bitumen. Donath¹⁸⁸ stated that benzene would yield more than 30 percent extract from brown coals but only 0.5 to 1 percent with bituminous coals, the solution in the latter case being fluorescent.

¹⁸⁶ Bone, W. A., Pearson, A. R., Sinkinson, E., and Stockings, W. E., *Proc. Roy. Soc. (London)*, **100A**, 582-98 (1922). Bone, W. A., Pearson, A. R., and Quarendon, R., *ibid.*, **105A**, 608-25 (1924). Bone, W. A., Horton, L., and Tei, L. J., *ibid.*, **120A**, 523-45 (1928).

¹⁸⁷ Fischer, F., Broche, H., and Strauch, J., *Brennstoff-Chem.*, **5**, 299-301 (1924), **6**, 33-43 (1925).

¹⁸⁸ Donath, E., *Braunkohle*, **25**, 315-19 (1926).

Davis and Reynolds¹⁹² investigated the benzene-pressure extraction of six different kinds of coal that are industrially coked. Kester¹⁹³ discussed the significance of solvent analysis applied to coal and the lack of unity and standardization in the work which has been done to date. (See Chapter 19.)

Extraction with Alkalies. Stansfield and Gilbert¹⁹⁴ fused coals with solid KOH with exclusion of air and determined the extracted ulmins by precipitation or titration. There was little differentiation between anthracitic and bituminous coals, but the sol-

¹⁸⁹ Rose, H. J., and Hill, W. H., U. S. Pat. 1,925,005 (1933).

¹⁹⁰ Rose, H. J., and Hill, W. H., Fr. Pat. 660,177 (1929).

¹⁹¹ Gillet, A., and Pirlot, A., *Bull. soc. chim. Belg.*, **41**, 511-20 (1932); *Fuel*, **15**, 124-7 (1936).

¹⁹² Davis, J. D., and Reynolds, D. A., *Ind. Eng. Chem.*, **21**, 1295-8 (1929).

¹⁹³ Kester, E. B., *Fuel*, **10**, 277-85 (1931).

¹⁹⁴ Stansfield, E., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 165-9 (1932); *Fuel*, **11**, 347-9 (1932).

uble ulmins differentiated lower-rank coals much more strikingly than ordinary chemical analyses, apparently emphasizing geological age rather than rank.

European investigators have frequently used alkali extraction to differentiate between peat, brown coal, lignite, and bituminous coal.^{195, 196} The second part of reference 195 describes the examination of a number of specimens and contains a bibliography of papers dealing with the reactions and properties of peat and brown coal. The proportions of pentosans in peat and brown coal were found to differ greatly and to afford a means of differentiation. The reducing effect of peat extracts is a qualitative reaction.^{93, 197}

Zhemchuzhnikov and Ergol'skaya,¹⁹⁸ in discussing a proposal of Koshkin and Tokarev,¹⁹⁹ stated that classification of coals by the content of humic acids extracted under pressure of 25 atmospheres with alkali is not justified because of other reactions which may occur.

Adsorption. Moore and Sinnatt²⁰⁰ studied the retention of aromatic hydrocarbon vapors by anthracite, bituminous coal, peat, gas coke, and charcoal. Chorazy²⁰¹ found that the adsorption of pyridine vapor by coal was inversely proportional to the carbon-to-hydrogen ratio up to 20, beyond which adsorption was insignificant. Petrographic constituents were

included in the study. The quantity of pyridine vapor adsorbed was closely proportional to the content of pyridine-extractible substances. This was confirmed by Bunte, Brückner, and Simpson,²⁰² who likewise believed that the degree of coalification may be measured by methods based on colloidal properties of the coal. Maier and Tsukerman²⁰³ determined adsorptive ability for pyrimidine vapor.

Pentegov and Nyankovskii^{204, 205} differentiated brown and bituminous coals by their adsorptive powers for oxalic acid, ferric chloride, and methylene blue, and correlated adsorption with gas yield, ether-soluble hydrogenation products, weathering, and spontaneous combustion.

Starzewska²⁰⁶ correlated methylene blue adsorption with rank, the greatest adsorption being for noncaking, gas-flame coals. Petrographic constituents were included in the tests. Maier and Tsukerman²⁰³ stated that methylene blue adsorption can be utilized only for low-rank coals which have no caking properties. Ermolenko and Ginzburg²⁰⁷ studied the adsorption activity of peat, brown coal, and anthracite with iodine and oxalic acid. Syskov and Ushakova²⁰⁸ reported that the nature and degree of oxidation of a coal can be evaluated by its adsorbing power towards aqueous barium hydroxide, with results intermediate between those of the fresh coal and lignite, but that

195 Strache, H., *Brennstoff-Chem.*, **3**, 311-2 (1922). Donath, E., and Lissner, A., *Braunkohle*, **27**, 257-64 (1928).

196 Gothan, W., *ibid.*, **24**, 1128-35 (1926).

197 Gothan, W., Pietsch, K., and Petrascheck, W., *ibid.*, **26**, 669-74 (1927). Dolch, M., and Dietzel, E., *Z. oberschles. berg- u. hüttenmänn. Ver. Katowice*, **68**, 118-24 (1929).

198 Zhemchuzhnikov, Y. A., and Ergol'skaya, Z. V., *Khim. Tverdogo Topliva*, **7**, 513-6 (1936).

199 Koshkin, N. V., and Tokarev, V. P., *ibid.*, **7**, 516-20 (1936).

200 Moore, B., and Sinnatt, F. S., *Fuel*, **6**, 312-8 (1927).

201 Chorazy, M., *Przemysl Chem.*, **15**, 233-70 (1931).

202 Bunte, K., Brückner, H., and Simpson, H. G., *Fuel*, **12**, 268-70 (1933).

203 Maier, L. M., and Tsukerman, L. E., *Khim. Tverdogo Topliva*, **8**, 647-62 (1937).

204 Pentegov, B. P., and Nyankovskii, R. N., *Pub. Far East. State Univ. (Vladivostok)*, **7**, No. 6 (1927), 18 pp.

205 Pentegov, B. P., *ibid.*, **7**, No. 12, 1929, pp. 3-28.

206 Starzewska, H., *Przemysl Chem.*, **18**, 556-60 (1934).

207 Ermolenko, N. F., and Ginzburg, D. Z., *Belaruskaya Akad. Navuk. Inst. Khim. Sbornik Prats.*, **1**, 143-65 (1934).

208 Syskov, K. I., and Ushakova, A. A., *Khim. Tverdogo Topliva*, **8**, 692-702 (1937).

aqueous solutions of iodine, oxalic acid, or methylene blue are not suitable for this purpose.

Stadnikoff and Proskurnina²⁰⁹ suggested the adsorption of ferric hydroxide from aqueous ferric chloride as a quantitative means of defining peat, lignite, and coal. Kreulen²¹⁰ pointed out that the size of particles must be standardized in this test. Pentegov and Nyankovskii²⁰⁴ stated that determinations using ferric chloride or methylene blue but not oxalic acid must be made with freshly pulverized coal, as the adsorptive capacity varies greatly with storage. Springer and Abele²¹¹ believed that the adsorption of ferric chloride is an unreliable index for the differentiation of peat and lignite, and they preferred to use the pentosan content, which is very rarely less than 2 percent for peat or greater than 1 percent for lignite. Krym and Panchenko²¹² presented results to show that the action of coal on ferric chloride is reduction rather than adsorption of ferric hydroxide.

Wet Oxidation. Francis and Wheeler²¹³ pointed out that the "rational analysis" of coal in terms of free hydrocarbons, resinous compounds, organized plant entities, and ulmin compounds is not sufficient to specify the quality of the coal. It is also necessary to take into account the fact that the ulmin compounds vary in composition from coal to coal. The percentage of soluble products produced by treatment with potassium chlorate determines the reactivity index, which is related to the carbon content of

coals. Francis and Morris²¹⁴ investigated the oxidizability by several agents of American coals from thirty-two sources, varying from lignite to low-volatile bituminous in rank. They concluded that the quickest and probably the most accurate method of estimating the reactivity of coals is to determine the percentage rate of formation of soluble ulmins during pressure oxidation in an aqueous solution of hydrochloric acid and potassium chlorate. This procedure placed the coals in almost the same order as atmospheric oxidation. The higher the rank of coal, the harder it is to oxidize, with some exceptions for coals of low rank.

Francis⁵⁷ stated that the carbon content of the ulmin is a measure of the "rank" of the coal and that it can best be determined on the vitrain constituent, corrected for the resins and hydrocarbons present.

Kreulen^{215, 216} determined the oxidizability of thirty-six coals having 38.7 to 3.0 percent volatile matter, by means of potassium permanganate, and found that oxidation tended to decrease progressively with volatile matter. From tests on sixty coals he concluded that the humic acid factor varied from 0 to 360 and could be correlated with Btu, ultimate analysis, coking properties, and primary tar yield. Heathcoat²¹⁷ proposed the "permanganate number," determined with alkaline potassium permanganate, as a quick method for gaging the rank of coal. Olin and Waterman²¹⁸ found a marked correlation between the permanganate number of a coal and its rank. Thirty United States coals gave results ranging from 135 for a South Dakota lignite to 3 for a Pennsylvania an-

²⁰⁹ Stadnikoff, G., and Proskurnina, N., *Brennstoff-Chem.*, **7**, 197-9 (1926), **8**, 305-6 (1927).

²¹⁰ Kreulen, D. J. W., *ibid.*, **7**, 331-2 (1926).

²¹¹ Springer, U., and Abele, G., *ibid.*, **8**, 117-20 (1927).

²¹² Krym, V. S., and Panchenko, S. I., *ibid.*, **10**, 63-5 (1929).

²¹³ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **131**, 2967-79 (1928).

²¹⁴ Francis, W., and Morris, H. M., *U. S. Bur. Mines, Bull.* **340** (1931), 44 pp.

²¹⁵ Kreulen, D. J. W., *Brennstoff-Chem.*, **10**, 397-400 (1929).

²¹⁶ Kreulen, D. J. W., *ibid.*, **15**, 11-2 (1934).

²¹⁷ Heathcoat, F., *Fuel*, **12**, 4-9 (1933).

²¹⁸ Olin, H. L., and Waterman, W. W., *Ind. Eng. Chem.*, **28**, 1024-5 (1936).

thracite. Bone and associates²¹⁹ pointed out that the proportion of benzenoids after the alkaline permanganate oxidation of coals seemed to indicate that the proportions of benzenoids increase in the series peat to anthracite.

Juettner²²⁰ used nitric acid followed by alkaline permanganate solution for obtaining the maximum yield of mellitic acid (benzenehexacarboxylic acid) from six coals ranging from high-volatile bituminous to anthracite in rank, also from various cokes, carbons, and pitches. The yield of mellitic acid increased with rank. Kent⁷⁸ determined the humic acid yield by alkaline permanganate oxidation of low-hydrogen, low-rank coals from Australia.

Winter²²¹ referred to schungite and other naturally occurring substances intermediate between anthracite and graphite, stating that, like anthracite, it does not yield insoluble graphitic acid when oxidized with nitric acid and potassium chlorate. Gothan,¹⁹⁶ in describing tests for differentiating bituminous coal, brown coal, and peat, said that brown coals almost always give a positive "lignin test," that is, a red-colored liquid on boiling with dilute nitric acid. Petrascheck¹⁵⁸ stated that, in some cases, samples from the same brown coal deposits give different results in the lignin test. Donath¹⁸⁸ stated that brown coal is characteristically converted to humic acid at 70° C by dilute nitric acid. Bode²²² has proposed a modification of the test. Francis and Morris²¹⁴ investigated the nitric oxidation of American coals of various ranks.

²¹⁹ Bone, W. A., Parsons, L. G. B., Sapiro, R. H., and Grocock, C. M., *Proc. Roy. Soc. (London)*, **148A**, 492-522 (1935).

²²⁰ Juettner, B., *J. Am. Chem. Soc.*, **59**, 1472-4 (1937).

²²¹ Winter, H., *Glückauf*, **60**, 1-6 (1924).

²²² Bode, H., *Braunkohle*, **29**, 982-9 (1930).

Eccles and McCulloch²²³ chlorinated twenty-nine different coals and compared the results with Seyler's classification according to ultimate analysis.

Kidokoro and Shirane²²⁴ treated coal with a solution of sodium peroxide at 50 to 60° C, and another portion with concentrated sulfuric acid at 100° C, followed by an acid solution of potassium dichromate at room temperature. From the results they derived the "brown coal," "stone coal," and "anthracite coal" numbers, in order to identify rank. Experiments on oxidation and spontaneous combustion were included.

Slow Combustion. The literature on atmospheric weathering and combustion of coal, as related to rank, is too extensive for coverage here. (See Chapters 18 and 33.) Francis²²⁵ classified coals on the basis of ulmins produced by the oxidation of coal by dry air at 150° C, and also with nitric acid, using sixteen coals. Francis and Morris²¹⁴ also used atmospheric oxidation and nitric acid on a series of coals. Stansfield, Lang, and Gilbert²²⁶ investigated the effect of oxidation of coals of various ranks due to storage and oven-drying of samples used for analysis and presented results on metering the quantity of oxygen absorbed during the ball-milling of twenty-four coals ranging from medium-volatile bituminous to subbituminous C coal. In general, there was good correlation between oxygen absorption and rank of coal.

Kreulen's proposal²²⁷ to classify coals by means of the ignition temperature in oxy-

²²³ Eccles, A., and McCulloch, A., *Fuel*, **10**, 308-19 (1931).

²²⁴ Kidokoro, T., and Shirane, G., *J. Fuel Soc. Japan*, **9**, 43-9 (1930).

²²⁵ Francis, W., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 438-56 (1930).

²²⁶ Stansfield, E., Lang, W. A., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 243-54 (1934); *Fuel*, **15**, 12-4 (1936).

²²⁷ Kreulen, D. J. W., *Chem. Weekblad*, **29**, 201-4 (1932).

gen has been critically discussed by Pieters and Koopmans.²²⁸

Hydrogenation. The U. S. Bureau of Mines has systematically investigated the hydrogenation of all ranks and types of bituminous coals, as well as petrographic constituents.^{84, 35, 59, 229} These papers give the source, proximate and ultimate analysis of the coals hydrogenated, hydrogenation data and yields, and the composition of the gases, distillates, pitches, and residues obtained. The yields of primary tar or pitch from anthraxylon (vitrain) were directly proportional to the carbon content of the original samples up to about 89 percent carbon, but coals with more than 89 percent carbon on the dry, ash-free basis were less easily liquefied. Even when the average carbon content of a coal is low, its opaque constituents—opaque attritus and fusain—have a high carbon content and are incompletely liquefied. Yields can be predicted from a knowledge of rank and petrographic composition. About the same amount of hydrogen is required to liquefy coals, regardless of rank, but the amount and nature of the products obtained vary.

Warren, Bowles, and Gilmore²³⁰ have reported results of hydrogenation tests on nine Canadian coals ranging from lignite to medium-volatile bituminous rank. With one exception, the rank of coal had a fairly consistent influence on the yields. For additional information on coal hydrogenation, see the separate chapter on this subject

(Chapter 38), and the extensive bibliographies in the above references.

Friability and Grindability of Coal. Various tentative standard methods are available for comparing the strength of coals. These cover the drop shatter test,²³¹ the tumbler test,²³² the grindability by ball mill,²³³ and Hardgrove-machine²³⁴ methods. (See Chapter 5.) Many articles have been published in connection with the development of these methods, which are still tentative and are being actively studied for revision. Weathering or slacking properties have already been mentioned, and coal sizes in relation to commercial classification will be discussed later.

Pishel²³⁵ studied the adherence of coals to an agate mortar when ground, and from tests on 150 samples ranging from lignite to anthracite proposed this as a test for coking properties.

Color. Campbell,¹⁴⁸ in 1908, suggested color for the separation of lignite and sub-bituminous coals, the former being brown and the latter black. He objected to the use of the brown streak test as including both lignite and subbituminous and probably some bituminous coals. Bode^{93, 222} and Gothan¹⁹⁶ referred to the streak on porcelain, which is usually black for bituminous coals and brown or brownish black for coals of lower rank.

Reflectivity. Hoffmann and Jenkner²³⁶ observed vitrain by reflected light under the microscope with a microphotometer, and they concluded that reflection was directly proportional to coalification. Under

²²⁸ Pieters, H. A. J., and Koopmans, H., *ibid.*, **30**, 374-5 (1933).

²²⁹ Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., and Storch, H. H., *Fuel*, **18**, 132-41, 196-203 (1939); *Ind. Eng. Chem.*, **31**, 190-5, 1155-61 (1939). Eisner, A., Sprunk, G. C., Clarke, L., Fisher, C. H., and Storch, H. H., *ibid.*, **32**, 73-8 (1940). Storch, H. H., Hirst, L. L., Fisher, C. H., Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 622* (1941), 110 pp.

²³⁰ Warren, T. E., Bowles, K. W., and Gilmore, R. E., *Ind. Eng. Chem.*, **31**, 1021-5 (1939).

²³¹ *Am. Soc. Testing Materials, Standards*, Pt. III, D440-37T, p. 570, 1939.

²³² *Ibid.*, D441-37T, p. 576.

²³³ *Ibid.*, D408-37T, p. 562.

²³⁴ *Ibid.*, D409-37T, p. 566.

²³⁵ Pishel, M. A., *Econ. Geol.*, **3**, 265-7 (1908).

²³⁶ Hoffmann, E., and Jenkner, A., *Glückauf*, **68**, 81-8 (1932). Hoffmann, E., *ibid.*, **68**, 523 (1932). Jenkner, A., and Hoffmann, E., *Brennstoff-Chem.*, **13**, 181-7 (1932).

polarized light, coal sections of increasing rank exhibited an increasing anisotropy. Polarized light was also advantageous for the detection of durain. Zhemchuzhnikov²³⁷ found that coal luster increased with decreasing volatile matter. A volatile matter range of 2 to 46 percent was investigated. (See Chapter 7.)

Other Physical Constants. McCabe⁵⁸ studied physical evidence of the development of rank in vitrain, or anthraxylon, in fifteen coals, mostly high-volatile bituminous A, B, and C coals from Illinois, but including lignite, subbituminous, and medium-volatile bituminous coals. He found that the angle of polarization and refractive index varied systematically with rank. X-ray diffraction patterns and electrical resistivities were determined. Corrie²³⁸ found that X-ray patterns were an efficient means of distinguishing between peranthracites, which have a marked crystalline structure, and anthracites. (See Chapter 7.)

Ewing and associates²³⁹ determined that the electrical resistance of solid specimens of Pennsylvania anthracite varied more than a million times over a range in volatile matter of 9.5 to 3.5 percent. Semi-anthracite of 9.5 percent volatile matter had high resistivity similar to a sample of 27 percent volatile matter bituminous coal. Lebeau²⁴⁰ studied the electrical and many other properties of peranthracites and anthracites. Sinnatt and Macpherson²⁴¹

published values for the thermal conductivity and specific heat of various coals and associated materials.

CLASSIFICATION BY GRADE

A.S.T.M. standard specifications for classification of coals by grade¹³⁵ cover quality as determined by size, calorific value, ash content, ash-softening temperature, and sulfur.

Size is designated in accordance with an A.S.T.M. standard method,¹³⁶ which should be consulted for details. The calorific value is expressed in hundreds of Btu to the nearest hundred, on the basis of coal as sampled. The remaining symbols for grading coal are summarized in Table XV.

The standard specifications for classification of coals by rank and by grade provide symbols for presenting a condensed description of the coal. Thus,

(62-146), 2-4 in., 132-AS-F24-S1.6

refers to a high-volatile A bituminous coal having 61.5 to 62.4 percent fixed carbon on the dry, mineral-matter-free basis, and 14,550 to 14,649 Btu on the moist, mineral-matter-free basis. Round-hole screens would retain more than 80 percent by weight of the sample between 2- and 4-inch screens. The Btu as sampled ranged between 13,150 and 13,249, the ash between 6.1 and 8.0 percent, the ash-softening temperature between 2,400 and 2,590° F, and the sulfur between 1.4 and 1.6 percent, inclusive. Further reference to grade classification is included later in this chapter under marketing practice.

CLASSIFICATION ACCORDING TO USE

Coals of various types, ranks, and grades have very different degrees of suitability for specific uses and types of equipment. Since a variety of coals are available in most industrial regions, there has been a

²³⁷ Zhemchuzhnikov, Y. A., *Inst. Mekhanicheskoi Obrabotki Poleznuiikh Iskopaemuikh "Mekhanobr," 15 yrs. Socialistic Ind. Service, 1*, 37-51 (1935).

²³⁸ Corrie, P., *Compt. rend.*, **199**, 410-2 (1934).

²³⁹ Ewing, M., Crary, A. P., Peoples, J. W., and Peoples, J. A., Jr., *Trans. Am. Inst. Mining Met. Engrs.*, **119**, 472-6 (1936).

²⁴⁰ Lebeau, P., *Compt. rend.*, **197**, 1234-6 (1933).

²⁴¹ Sinnatt, F. S., and Macpherson, H., *Fuel*, **3**, 12-4 (1924).

TABLE XV

SYMBOLS FOR GRADING COAL ACCORDING TO ASH, SOFTENING TEMPERATURE OF ASH, AND SULFUR WHERE ANALYSES ARE EXPRESSED ON BASIS OF THE COAL AS SAMPLED.¹³⁵

Ash *		Softening Temperature of Ash †		Sulfur *	
Symbol	Percent, ‡ Inclusive	Symbol	Degrees Fahrenheit, Inclusive	Symbol	Percent, Inclusive
A4	0.0 to 4.0	F28	2,800 and higher	S0.7	0.0 to 0.7
A6	4.1 to 6.0	F26	2,600 to 2,790	S1.0	0.8 to 1.0
A8	6.1 to 8.0	F24	2,400 to 2,590	S1.3	1.1 to 1.3
A10	8.1 to 10.0	F22	2,200 to 2,390	S1.6	1.4 to 1.6
A12	10.1 to 12.0	F20	2,000 to 2,190	S2.0	1.7 to 2.0
A14	12.1 to 14.0	F20 minus	less than 2,000	S3.0	2.1 to 3.0
A16	14.1 to 16.0			S5.0	3.1 to 5.0
A18	16.1 to 18.0			S5.0 plus	5.1 and higher
A20	18.1 to 20.0				
A20 plus	20.1 and higher				

* Ash and sulfur shall be reported to the nearest 0.1 percent by dropping the second decimal figure when it is 0.01 to 0.04, inclusive, and by increasing the percentage by 0.1 percent when the second decimal figure is 0.05 to 0.09, inclusive. For example, 4.85 to 4.94 percent, inclusive, shall be considered to be 4.9 percent.

† Ash-softening temperatures shall be reported to the nearest 10 F; for example, 2,635 to 2,644 F, inclusive, shall be considered to be 2,640 F.

‡ For commercial grading of coals, ranges in the percentage of ash smaller than 2 percent are commonly used.

continuing effort throughout the world to correlate chemical and physical factors as determined in the laboratory with practical operating results, in order to facilitate the selection of coals for each use.

The most comprehensive undertaking has been a report²⁴² on technical factors recommended for consideration in the selection of coal and their relative importance, which was prepared in connection with the work of A.S.T.M. coal-classification committees. All uses of coal were divided into 25 principal categories, which were further subdivided into 183 specialized uses or conditions of use. Each of these was then considered with respect to 33 different coal-selection factors (e.g., rank, grade,

moisture, ash, sulfur, size, weathering, etc.), which were rated in four degrees from "very essential" to "not important." The resulting ratings, which cover some 6,000 items, were based on opinions obtained by the questionnaire method from technical experts familiar with the various uses.

Though this report indicates the relative importance of each coal-selection factor for the various uses or operating conditions, it does *not* give any numerical limits. For example, in bituminous coal to be burned on a chain grate stoker under excessive load, the correct size and caking properties are stated to be "very essential," but there is no suggestion as to what the size or caking properties should be. In such coal, also, moisture is considered to be of "more than ordinary importance," ash-softening temperature is of "ordinary importance,"

²⁴² Anon., "Factors Recommended for Consideration in the Selection of Coal," No. 21, 2nd Ed., Nat. Assoc. Purchasing Agents, 11 Park Place, New York, N. Y., 1936, 21 pp.

and sulfur percentage is "not important." Reference is made to test methods or specifications whereby the various factors used in coal selection can be measured for particular coals.

This report does not show the buyer what coal to select, but it does serve as a detailed check list which points out the factors which need to be given special consideration, as well as the factors which are less important or unimportant when writing specifications. It was considered impractical to set up numerical limits for each factor and operating condition. No ready-made classification can replace the judgment of an experienced combustion engineer or fuel technologist who is able to combine technical aspects with the economic factors which apply at each individual plant. Full-scale plant tests are often necessary before a final decision is made.

Publications classifying or describing the factors important to each use of coal are far too numerous for comprehensive review here, and only a few will be mentioned.

Steam Generation. Flagg²⁴³ in discussing the classification of coal from the standpoint of the steam power consumer has pointed out that it is possible to design and construct stationary boiler plants so that they can be operated with whatever coal is the most economical supply therefor. However, once a plant is built, it should be supplied with fuel of appropriate quality, depending upon the type of equipment and operating conditions which exist.

In 1934, a joint committee on fuel values, consisting of seventeen A.I.M.E. and A.S.M.E. members, reported:

After careful consideration of the combination of qualities of coal available, the va-

riety of plant characteristics, and the interrelation of these factors, the Committee is convinced that it is impossible to set up any scale of values, or to devise any formula for general application that will accurately reflect the relative values of different coals for steam generation.²⁴⁴

The report lists a large number of factors which need to be considered when evaluating coal for a particular plant.

Barkley and Burdick²⁴⁵ correlated the agglutinating value of twenty-five coals with their coking action in natural- and forced-draft equipment, both hand- and stoker-fired. They concluded that agglutinating values can serve the experienced user in anticipating coal-burning characteristics.

Ostborg, Limbacher, and Sherman²⁴⁶ reported that, in checking the performance of coals on large underfeed stokers, an electric utility company uses the British standard method for the crucible swelling test for coal. Macfarlane and McAuliffe²⁴⁷ have discussed classification of railroad fuels, and their selection and use. Nicholls and others²⁴⁸ discussed the selection of all ranks of solid fuels for household use and their performance in house-heating boilers. Rose and Lasseter²⁴⁹ graphically studied the smoke-producing tendencies in coals of various ranks, including data from the preceding reference.

²⁴⁴ Gould, G. B., *Mining and Met.*, **16**, 62-4 (1935).

²⁴⁵ Barkley, J. F., and Burdick, L. R., *Power Plant Eng.*, **38**, 132-4 (1934).

²⁴⁶ Ostborg, H. N., Limbacher, H. R., and Sherman, R. A., *Am. Soc. Testing Materials, Preprint SI* (1942), 14 pp.

²⁴⁷ Macfarlane, M., *Trans. Am. Soc. Mech. Engrs.*, **50**, 157-60 (1928). McAuliffe, E., and Macfarlane, M., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 461-4 (1930).

²⁴⁸ Nicholls, P., Flagg, S. B., and Augustine, C. E., *U. S. Bur. Mines, Bull.* **276** (1928), 70 pp. Nicholls, P., *Trans. Am. Soc. Heat. Vent. Engrs.*, **45**, 257-68 (1939).

²⁴⁹ Rose, H. J., and Lasseter, F. P., *ibid.*, **45**, 329-38 (1939).

²⁴³ Flagg, S. B., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 477-80 (1930).

Rose²⁵⁰ compared the characteristics of anthracite with other domestic fuels.

Seyler⁸⁴ correlated his classification according to ultimate analyses with such factors as proximate analysis and Btu, flame temperature and intensity, and volume of flue gases. King and Frisby have discussed the selection of industrial coal from the English standpoint.²⁵¹ Matyushenko²⁵² has discussed the industrial classification of coals, based on a study of 2,200 Russian coals, which included the determination of various chemical and physical factors, a special burning test on grates to determine the reactivity and degree of deformation of coal under heat, and resistance to thermal shock.

Gas Manufacture. Fulweiler and Francklyn discussed the classification of coals used by the gas industry.²⁵³ Pettyjohn²⁵⁴ has reported on the evaluation of bituminous coals for use in water-gas generators. This included the results of chemical analysis, shatter, agglutinating, and thermal-shock tests on eighteen gas coals. Wright, Newman, and Gauger²⁵⁵ have investigated the resistance of anthracite to mechanical and thermal shock, primarily in connection with its use as water-gas fuel. Reference has already been made^{131, 132, 133} to formulas which are intended to indicate the quality of gas obtainable by carbonizing

coal. Mott²⁵⁶ assessed the value of gas coals.

Davies and Jones, Edgecombe, and Mott and Spooner have described methods for determining traces of tars yielded by fuels used in mobile gas producers.²⁵⁷ Ward and Morison²⁵⁸ discussed the characteristics desired in fuels for this use.

Coking Properties. The caking or agglomerating properties of bituminous coals have been used for classification purposes for more than a century. Karsten,⁶⁵ in 1826, classified such coals on the basis of the appearance of coke residue after heating into sand, sinter, and coking coals. Regnault⁶⁶ in 1837 described the appearance of the residue from the volatile-matter test on coals of all ranks. Richardson,²⁵⁹ in 1849, discussed the qualities of the coke residue as a basis of classification. Schondorff,²⁶⁰ in 1875, distinguished between sand coal, sintered sand coal, sinter coal, coking sintered coal, and coking coal. Seyler²⁶¹ preferred the terms discrete, semi-accretive, accretive, semi-concretive, and concretive to the above, or to the terms dry, lean, poor, rich, and fat.

Bauer²⁶² in 1908 tested the usefulness of the crucible method, as did Gruner and Bousquet,⁵ and Muck²⁶³ concluded that the yield as well as the nature of coke must

²⁵⁶ Mott, R. A., *Gas J.*, **205**, 33-4, 88-90 (1934).

²⁵⁷ Davies, R. G., and Jones, W. I., *Fuel*, **19**, 79-80 (1940). Edgecombe, L. J., *ibid.*, **19**, 201-3 (1940). Mott, R. A., and Spooner, C. E., *ibid.*, **20**, 71-3 (1941).

²⁵⁸ Ward, S. G., and Morison, W. J., *J. Inst. Fuel*, **15**, 131-46 (1942).

²⁵⁹ Richardson, J., *Inst. Civil Eng. (London), Minutes of Proc.*, **3**, 98 (1849).

²⁶⁰ Schondorff, A., *Z. Berg-, Hütten- u. Salinenwesen*, **23**, 135-62 (1875).

²⁶¹ Seyler, C. A., *Fuel*, **3**, 15-26, 41-9, 79-83 (1924).

²⁶² Bauer, A., thesis, Rostock, 1908.

²⁶³ Hinrichsen, F. W., and Taczak, S., *Die Chemie der Steinkohle*, W. Engelmann, Leipzig, 1916, 3rd Ed., p. 231.

²⁵⁰ Rose, H. J., *Trans. Ann. Anthracite Conf. Lehigh Univ.*, **1935**, 25-38, **1939**, 27-44; *Ind. Eng. Chem.*, **33**, 846-50 (1941).

²⁵¹ King, J. G., *Fuel Economist*, **5**, 19-22 (1929). Frisby, B., *Steam Engr.*, **3**, 137-9 (1934).

²⁵² Matyushenko, P. S., *Fuel*, **20**, 162-72 (1941).

²⁵³ Fulweiler, W. H., *Trans. Am. Inst. Mining Met. Engrs., Coal Div.*, **88**, 467-72 (1930). Francklyn, G., *ibid.*, **88**, 706-12 (1930).

²⁵⁴ Pettyjohn, E. S., *Proc. Am. Gas Assoc.*, **1930**, 1535-63.

²⁵⁵ Wright, C. C., Newman, L. L., and Gauger, A. W., *Penna. State Coll., Mineral Ind. Exp. Sta., Bull.* **31** (1941), 28 pp.

be used in properly classifying coking and sand coals.

Bode⁹³ in 1931 stated:

In Germany, advance beyond this system, which is only useful in general for bituminous coals, has not been made, although it has been repeatedly shown that the system is practically and scientifically of little value.

Seyler²⁶¹ published the carbon and hydrogen contents of many British and European coals, with comments on coking power, bitumen index, nature of coke, etc. Qvarfort²⁶⁴ proposed a laboratory coking test in which the final index number assigned to the coal is the summation of numbers representing the crushing strength, porosity, yield, etc. Meurice²⁶⁵ classified coal by its agglutinating index, procedure for determining which was given, and its index of coke production. Tables of data obtained with coals from various sources were included. Pettyjohn²⁵⁴ determined agglutinating and other physical values on eighteen gas coals. Iki¹⁸⁵ correlated the caking index of twenty-three Japanese coals with many other physical and chemical properties. Yancey, Johnson, and Selvig^{151, 152} determined the agglutinating value and many other properties of coals from Washington and other states. Selvig, Beattie, and Clelland²⁶⁶ studied the effect of many variables in determining the agglutinating value of coals mixed with sand. Davies, Mott, and Spooner²⁶⁷ described the Sheffield Laboratory Coking Test and correlated results with carbon and hydrogen percentages.

The British standard crucible swelling

²⁶⁴ Qvarfort, S., *Gas- u. Wasserfach*, **67**, 728-30 (1924); *Fuel*, **4**, 154-60 (1925).

²⁶⁵ Meurice, A., *Ing. chim.*, **17**, 131-55 (1929).

²⁶⁶ Selvig, W. A., Beattie, B. B., and Clelland, J. B., *Am. Soc. Testing Materials, Proc.*, **33**, Pt. II, 741-60 (1933).

²⁶⁷ Davies, R. G., and Mott, R. A., *Fuel*, **12**, 294-303 (1933). Mott, R. A., and Spooner, C. E., *ibid.*, **16**, 4-14 (1937).

test for coal²⁶⁸ issued in 1938 was found by Ostborg, Limbacher, and Sherman²⁴⁶ and by McCabe, Konzo, and Rees⁵⁰ to correlate with the coking behavior of bituminous coals in domestic underfeed stokers. Agglutinating and plasticity tests were also made. Gilmore, Connell, and Nicolls¹⁴⁵ discussed agglutinating and agglomerating tests for classifying weakly caking coals. Fish²⁶⁹ determined the agglutinating value of low-volatile Virginia coals, and Olin²⁷⁰ determined agglutinating values and other properties for Iowa coals.

Davis and associates²⁷¹ compared the plastic properties of coking coals by various methods. Pieters, Koopmans, and Hovers²⁷² studied the effect of rank and other variables on the plasticity of heated coal. Seyler^{84, 85} discussed plasticity and coking properties in relation to classification. Ramzin^{117, 153} used the nature of the coke, with other characteristics, in classifying Russian Donets Basin coals.

A series of publications of the U. S. Bureau of Mines, detailing the analysis and physical properties of coals and the quality of coke and byproduct yields obtained from various United States coals at a variety of temperatures, has been indexed by Wilson and Davis.¹¹ This covers the most comprehensive collection of comparable data that is available. It has been correlated by statistical methods by Lowry, Landau, and Naugle.²⁷³ The Fuel Research

²⁶⁸ Anon., *British Standard Method for the Crucible Swelling Test for Coal*, British Standards Institution, No. 804-1938, July, 1938.

²⁶⁹ Fish, F. H., *Virginia Polytech. Inst., Eng. Expt. Sta. Series, Bull.* **20** (1935), 14 pp.

²⁷⁰ Olin, H. L., *Fuel*, **16**, 304-9 (1937).

²⁷¹ Davis, J. D., Jung, F. W., Juettner, B., and Wallace, D. A., *Ind. Eng. Chem.*, **25**, 1269-74 (1933).

²⁷² Pieters, H. A. J., Koopmans, H., and Hovers, J. W. T., *Fuel*, **13**, 82-6 (1934).

²⁷³ Lowry, H. H., Landau, H. G., and Naugle, L. L., *Am. Inst. Mining Met. Eng., Tech. Pub.* **1332** (1941), 30 pp.

Survey papers¹² have presented data for British coals. Information on Canadian coals is available in various publications of the Canada Department of Mines, Mines Branch, Division of Fuels and Fuel Testing.

Fieldner and Davis²⁷⁴ have correlated chemical and physical tests, and Sprunk and Thiessen²⁷⁵ have correlated microscopic composition of coal, with coking properties and byproduct yields. Kühlwein²⁷⁶ classified coals according to petrographic structure and discussed the chemical behavior and carbonization yields of the banded constituents.

Fieldner and associates²⁷⁷ discussed high-temperature carbonizing properties, and Selvig and Ode²⁷⁸ evaluated laboratory assay tests for gas, coke, and byproduct yields. Yancey, Johnson, and Selvig¹⁵¹ published low-temperature carbonization yields for coals from Washington and other states. Dolch and Gerstendörfer²⁷⁹ found a definite relationship between the composition of the carbonization gases and age of the coals studied. Mott and associates²⁸⁰ have published extensive studies on coke formation correlated with rank, petrographic composition, etc.

²⁷⁴ Fieldner, A. C., and Davis, J. D., *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 540-86 (1931).

²⁷⁵ Sprunk, G. C., and Thiessen, R., *Ind. Eng. Chem.*, **27**, 446-51 (1935).

²⁷⁶ Kühlwein, F. L., *Tech. Mitt. Krupp*, **30**, 305-18 (1937).

²⁷⁷ Fieldner, A. C., Davis, J. D., Reynolds, D. A., and Holmes, C. R., *Ind. Eng. Chem.*, **26**, 300-3 (1934).

²⁷⁸ Selvig, W. A., and Ode, W. H., *Ind. Eng. Chem., Anal. Ed.*, **7**, 88-93 (1935).

²⁷⁹ Dolch, M., and Gerstendörfer, G., *Brennstoff-Chem.*, **3**, 225-31 (1922).

²⁸⁰ Mott, R. A., *Fuel*, **6**, 217 (1927), **12**, 185-94, 412-8 (1933), **13**, 356 (1934). Mott, R. A., and Shimmura, T., *ibid.*, **7**, 472-86 (1928). Burdekin, L., and Mott, R. A., *ibid.*, **12**, 232-9 (1933). Brewin, W., and Mott, R. A., *ibid.*, **12**, 239-42 (1933). Allinson, J. P., and Mott, R. A., *ibid.*, **12**, 258-68 (1933). Davies, R. G., and Mott, R. A., *ibid.*, **12**, 294-303, 330-40, 371-82 (1933).

Ralston⁸² and Rose⁹⁴ have graphically presented the ultimate analysis limits of coking coals. White⁸⁸ studied their hydrogen-to-oxygen ratio. Burrough, Swartzman, and Strong¹³³ classified coals for the byproduct coking industry by the specific volatile index, the calculated heating value of 1 percent volatile matter. The Midland Coke Research Committee⁷⁷ has studied the classification of English coals for coke making, on the basis of ultimate analysis, calorific value, etc. Bennett²⁸¹ believed that eventually all coals down to 80 percent carbon on the dry, ash-free basis would be found suitable for coke manufacture. Kreulen²¹⁶ correlated humic acid factor with coking properties. Rose and Sebastian²⁸² studied the change in analysis and swelling properties of coking coals due to oxidation at 80° C.

Other Uses. Many other references are available on coal selection for special uses. For example, Rice and Reid have discussed the properties of coal which affect its use for the ceramic and portland-cement industries, respectively.²⁸³ Williams²⁸⁴ summarized qualities of coal and coke required in nonferrous metallurgy.

COMMERCIAL CLASSIFICATION OF COAL

As would be expected in the case of a commodity so widely used and variable as coal, a great many trade classifications have been recognized or proposed. Reference will be made to only a few. The greatest interest centers in those classifications which are, or have been, officially enforced in some manner.

²⁸¹ Bennett, J. G., *J. Inst. Fuel*, **15**, 82-92 (1942).

²⁸² Rose, H. J., and Sebastian, J. J. S., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 556-82 (1930).

²⁸³ Rice, W. E., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 247-55 (1932). Reid, H. P., *ibid.*, **101**, 256-9 (1932).

²⁸⁴ Williams, C. E., *ibid.*, **101**, 260-8 (1932).

"POOL" CLASSIFICATIONS OF TIDEWATER
COAL EXCHANGES

During the first World War, the so-called pool classification of the Tidewater Coal Exchange was organized as a war measure to assist the railroads in handling all bituminous coal shipped to Atlantic tidewater ports. Shortly after the war, separate exchanges were set up at certain eastern ports. Although these had a relatively short existence, pool classifications continued to be used to some extent by coal-trade publications and coal companies in quoting prices.

The system adopted by the exchanges was a classification of coal *mines* based primarily on the quality of the coal as shown by analysis and heating value, use, size, structure, and seam, but including producing district, railroad, and tidewater port. This was the first large-scale systematic attempt at commercial classification in the United States, and though the pool classifications served their general purpose in the emergency, they were often found to be inadequate, misleading, and the source of trouble and litigation. Snyder²⁸⁵ listed the terms used in classifying coal handled by the Tidewater, Newport News, Lambert's and Sewall's Point Coal Exchanges, together with many hundreds of analyses of pool coals. Payne²⁸⁶ discussed the source and quality of pool coals and the operation of the exchanges. De Graff²⁸⁷ disagreed with certain average analyses shown in the preceding reference. Wadleigh²⁸⁸ in a summary of United States and foreign commercial coal classi-

fications devoted thirteen pages to pool classifications.

The U. S. Bureau of Standards,²⁸⁹ in 1930, sponsored the simplification of sizes and terminology of high-volatile bituminous coal handled over docks at the American head of the Great Lakes.

NATIONAL RECOVERY ADMINISTRATION
MINIMUM FAIR PRICE LISTS

In 1933, divisional code authorities operating under the National Industrial Recovery Act established minimum fair price lists for bituminous coal and beehive coke. These were set forth in numerous mimeographed circulars, supplements, correction sheets, etc., issued by the code authorities. The printed booklets, "Code Prices," issued by the American Wholesale Coal Association in October, November, and December, 1933, and February, 1934, are convenient references for the short-lived minimum prices under the N.R.A.

The primary classification was into geographical divisions and subdivisions, some of which were further divided into districts or mines. The size of coal had an important part in the pricing and might be thought of as the second major factor in the classification. The market area into which a coal was shipped often had an important bearing on the mine price, the purpose being to maintain a balance of competition. In some divisions, there was price classification according to seams, or by the industrial uses to which the coals were put. Reference to specific limits of analysis were infrequent. There were numerous exceptions to provide for washed coal, stripping coal, specially treated coal, absorption of freight differentials, etc.

Coal classification under N.R.A. code authorities did not represent a single inte-

²⁸⁵ Snyder, N. H., *U. S. Bur. Mines, Bull.* **230** (1923), 174 pp.

²⁸⁶ Payne, H. M., *Coal Age*, **19**, 442-5, 490-4, 539-41 (1921).

²⁸⁷ De Graff, G. A., *ibid.*, **20**, 222-3 (1921).

²⁸⁸ Wadleigh, F. R., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 673-98 (1930).

²⁸⁹ *Natl. Bur. Standards U. S., Misc. Pub.* **113** (1930), 14 pp.

grated system with a definite technical basis. Instead, the various classifications were devised locally by the divisional code authorities and represented hurried attempts to devise commercially workable plans of establishing fair competitive prices and thus prevent ruinous price-cutting during a financial depression. The classification used by each division depended upon the complexity of the local situation and market competition.

PRICE REGULATION UNDER THE BITUMINOUS COAL ACTS

The major objective of government regulation of the bituminous coal industry during the 1930's was to fix minimum prices at the average cost of production, so that the industry as a whole could break even financially, instead of operating at a loss year after year. The Coal Conservation Act of 1935 was followed by the Bituminous Coal Act of 1937,²⁹⁰ which had a two-year extension upon its expiration in 1941.

After more than three years of preparation, minimum coal prices went into effect on October 1, 1940. The schedule covered all coal except Pennsylvania anthracite and lignite, representing 22 mining districts and 242 distinct market areas. It was said that this minimum price schedule contained approximately one-half million prices. The act provided that:

The minimum prices so proposed shall reflect, as nearly as possible, the relative market value of the various kinds, qualities, and sizes of coal, shall be just and equitable as between producers within the district, and shall have due regard to the interests of the consuming public.

Provision was made for fixing maximum prices, if necessary, and, owing to price

stiffening resulting from the wartime demand for coal, Office of Price Administration Orders 120 and 122 effective May 18, 1942, set a ceiling on prices and governed the retailing and wholesaling of bituminous coal.

Relative prices under the coal acts were arrived at from considerations of market history rather than of chemical and physical properties of the coal, with few exceptions. The general policy was to maintain the *status quo* of coal distribution, prices in a given district being determined by the freight origin group of the mine, the price classification (depending upon size, grade, etc.), the size group number, the "market area" of the destination, the method of transportation, and the use of the coal, together with numerous exceptions which altered the price. In general, under this classification a particular ton of coal has several distinct and different prices at the mine, depending upon the market in which it is to be sold, the method of transportation to be used, and the use to which it will be put. Provision was made for revision of minimum prices to remove inequalities, or when there were changes in weighted average cost of production amounting to more than two cents per ton.

A large mass of information relating to these prices has been issued, including supplements, revisions, and legal decisions. The current minimum prices are not all available under one cover, but a large volume issued by the National Coal Association²⁹¹ forms a convenient general reference to the subject.

In most of the principal coal-producing countries of the world, there is some form

²⁹⁰ Bituminous Coal Act of 1937, Public No. 48, 75th Congress, Chapter 127, 1st Session, H.R. 4985.

²⁹¹ Anon., "Coal Prices—Bituminous, Minimum Coal Prices as Established by the Coal Division of the Department of Interior, Effective Oct. 1, 1940," National Coal Association, Washington, D. C., 1940, with supplements.

of government control of the coal industry, through government ownership of the coal deposits, allocation of tonnage, price control, or other means. All these involve some type of commercial classification.

PENNSYLVANIA ANTHRACITE

Pennsylvania anthracite was not included in the above-mentioned commercial classifications. The anthracite producers have long maintained standards of preparation and tolerances relative to screen size and visible impurities in each commercial size. The current standards²⁹² contain definite maximum ash limitations for the buckwheat and rice sizes.

After a period of disastrous price competition, the anthracite producers began on January 29, 1940, to operate under a voluntary production control program in co-operation with state and labor representatives. Anthracite requirements were estimated each week, and each producer was allowed to produce a fixed percentage of the total quota. Upon the passage of state legislation on the subject, the plan was operated by the Anthracite Committee of the Production Control Plan for the Anthracite Industry, Harrisburg, Pa., under the Pennsylvania Department of Commerce.

This plan did not include price fixing but attempted to stabilize prices by maintaining a reasonable balance between production and demand. The federal Office of Price Administration issued orders putting a ceiling on anthracite mine prices as of March, 1942.²⁹³

Parker²⁹⁴ summarized the commercial

description of Pennsylvania anthracite in 1930.

LIGNITE

Lignite is not included in the above classifications. The characteristics of the lignites of the United States have been described by Lavine.²⁹⁵

CLASSIFICATION BY DISTRICT SELLING AGENCIES

Before federal regulation of bituminous coal prices was established, various co-operative regional agencies were formed to market coals and establish minimum prices for their members in selected mining areas. These agencies classified and graded coals of the member companies chiefly on the basis of their known suitability for various uses, as for power plants, byproduct coking, the manufacture of various types of gas, and as fuel for metallurgical, ceramic, cement burning, railroad and bunker, general steam, domestic, and other uses. A single coal was often suitable for several purposes, and thus had a multiple classification. Occasionally the agencies supported an extensive program of sampling and analysis of the various sizes of coal from each mine. Eavenson²⁹⁶ has described the classification of coals as practiced by the first of these agencies.

SIZE OF COAL

Examination of commercial classifications of coal from almost any country will show the great importance attached to size of lumps, since this is one of the determining factors in the selection of coal for

²⁹² Anon., *Saward's J.*, **23**, 532 (1941), **24**, 402, 443 (1941).

²⁹³ Office of Price Administration, Maximum Price Regulation 112, including Supplements 1 and 2, 1942.

²⁹⁴ Parker, E. W., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 699-705 (1930).

²⁹⁵ Lavine, I., *Fuel*, **20**, 14-9, 31-8, 48-51, 78-81, 117-21 (1941).

²⁹⁶ Eavenson, H. N., "Classification of Coals Sold through Appalachian Coals, Inc.," mimeo., 3 pp., attached to *Am. Soc. Testing Materials, Sectional Comm. on Classification Coal, Gen. Circ. 42* (1933).

many uses. Given,²⁹⁷ in 1932, tabulated the various sizes of coal produced in the different coal fields of the United States. Committee work on American Standard specifications for the classification of coals led to the preparation of a standard method for designating the size of coal from its screen analysis.¹³⁶ A standing subcommittee of the American Society for Testing Materials has jurisdiction over matters concerning coal-size designations.

The Bureau of Standards²⁹⁹ has given equivalent dimensions for bar and round-hole screens, also slotted plates. Yancey and Zane²⁹⁸ discussed the relationship of size percentages obtained in testing coal with round- and square-hole screens.

The American Society for Testing Materials has published a number of standard or tentative standard methods for testing the screen analysis of coal, its grindability, and strength according to the drop-shatter and tumbler tests. The latest edition of the A.S.T.M. Standards and subsequent yearly supplements should be consulted for such methods.

Coals tend to become broken in commercial handling, and much research has been done on this subject. Smith²⁹⁹ determined the friability of Illinois coals by drop-shatter test, and Lawall and Holland³⁰⁰ determined the friability by tumbler test, and other physical characteristics, of West Virginia coals. The U. S. Bureau of Mines⁵³ has investigated the power required to pulverize the petrographic constituents of an Illinois coal and has done much work on the general subject of coal friability and pulverization.

²⁹⁷ Given, I. A., *Coal Age*, **37**, 334-8 (1932).

²⁹⁸ Yancey, H. F., and Zane, R. E., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 295-8 (1934).

²⁹⁹ Smith, C. M., *Univ. Illinois, Eng. Exp. Sta., Bull.* **218** (1930), 24 pp.

³⁰⁰ Lawall, C. E., and Holland, C. T., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 100-13 (1932).

The Canadian Bureau of Mines³⁰¹ has made an extensive study of friability and grindability of coals sold in Canada. (See Chapter 5.)

MISCELLANEOUS ARTICLES ON COMMERCIAL CLASSIFICATION

Tryon³⁰² discussed classification from the viewpoint of the coal statistician. Harris³⁰³ and Rose³⁰⁴ discussed classification for purchasing agents.

Numerous federal and state publications have dealt with analyses of coal from particular states, and the use of such coal for specific purposes. No attempt will be made to mention the many valuable reports of this type, which are often quite specific and contain much experimental data on the use of coal for house heating, stokers, locomotives, power plants, etc.

Reports by geological surveys form another valuable source of information. For example, Cady³⁰⁵ is the author of a 354-page book on the classification and selection of Illinois coals.

The Federal Trade Commission, better business bureaus, and similar organizations interested in promoting truth in advertising and better business ethics have made numerous rulings relating to the names indicating origin, size, and quality of coal, etc., which may be used in retail coal ad-

³⁰¹ Nicolls, J. H. H., *Can. Dept. Mines, Mines Branch, Invest. Fuels and Fuel Testing*, No. 644, pp. 20-35, 1926. Gilmore, R. E., Nicolls, J. H. H., and Connell, G. P., *ibid.*, No. 762, 102 pp., 1935. Gilmore, R. E., and Nicolls, J. H. H., *Can. Bur. Mines, Mines & Geol. Branch, Dept. Mines & Resources, Memorandum Series No. 70*, 1939, 25 pp.

³⁰² Tryon, F. G., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 481-5 (1930).

³⁰³ Harris, T. W., Jr., *Purchasing Agent*, **19**, 1188-9 (1930); *Ind. Standardization*, **7**, 175 (1936).

³⁰⁴ Rose, H. J., *Purchasing Agent*, **19**, 735-6, 802 (1930).

³⁰⁵ Cady, G. H., *Illinois State Geol. Surv., Bull.* **62** (1935), 354 pp.

vertising. The general policy is to eliminate misleading terms. Court action has sometimes been taken to stop the use of terms which resulted in unfair competition.

COMMERCIAL CLASSIFICATION IN CANADA

Numerous references have already been made to Canadian work on coal classification. These may be supplemented as follows: Gilmore³⁰⁶ in 1930 discussed the status of coal classification in Canada, including systems used for customs tariff purposes. Haanel and Gilmore³⁰⁷ discussed testing, classification, and utilization studies of Canadian coals and included experimental data. The National Research Council of Canada's report recommending the application of the A.S.T.M. classifications to Canadian coals¹⁴⁴ has already been mentioned.

The Canadian Government Purchasing Standards Committee issued a tentative specification³⁰⁸ for coal in 1940, which included designations by class, group, and grade based on the A.S.T.M. classifications, designation of sizes, bases for comparing quotations and rejection or acceptance of deliveries, and examples of computing price adjustments. A more recent statistical report³⁰⁹ shows the exporter's designations and size of anthracites imported from nine countries.

CLASSIFICATION IN OTHER COUNTRIES

Wadleigh²⁸⁸ has tabulated commercial classifications used in various countries.

³⁰⁶ Gilmore, R. E., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 529-40 (1930).

³⁰⁷ Haanel, B. F., and Gilmore, R. E., *Fuel*, 17, 80-90, 109-18, 128-34 (1938).

³⁰⁸ Anon., National Research Council (Canada), Codes and Specifications Section, No. 18-GP-1-1940, Tentative, Feb. 12, 1940.

³⁰⁹ Anon., Dominion Bur. of Statistics (Canada), *Coal Statistics for Canada for the Calendar Year 1939*, 1941.

The following references will supplement those previously given.

In England, Wade, Mott, and Mitton and Davies have discussed the commercial evaluation, classification, and grading of coal.³¹⁰

Gruner and Bousquet⁵ gave the commercial names of coal sizes from various French producing areas, with a table of uses largely based on the size of coal. An official report³¹¹ on French coal described the confusion resulting from a multiplicity of names which were not reserved for specific qualities. It recommended that future commercial classification be based on geographical origin, nature (Gruner classification), and size, for which five ranges were suggested.

Bierbrauer³¹² classified Austrian coals on an ultimate analysis diagram. Blum³¹³ concluded that the decisive factors in determining the rank of Rumanian coals were ultimate analysis, behavior on carbonization, and the action of certain solvents.

The classification of Russian coals has received considerable attention. Krym³¹⁴ studied the proximate and ultimate analysis and Btu of coals from the Donets Basin. Ramzin's conclusions,¹⁵⁸ based on the study of 20,000 analyses representing all the principal regions of Russia, were summarized in a large table. In most fields the name of the coal is sufficient to define the coal, but in the Donets Basin, which is noted for the variety of its coals, the volatile matter

³¹⁰ Wade, C. F., *Colliery Eng.*, 4, 75-6 (1927). Mott, R. A., *Colliery Guardian*, 147, 811-4, 859-62 (1933). Mitton, H. E., and Davies, D. T., *Trans. Inst. Mining Engrs. (London)*, 90, 3-8, 45-61 (1935).

³¹¹ Anon., *Ann. mines*, 11, 1-421 (1937).

³¹² Bierbrauer, E., *Sparwirtschaft*, 14, 236-7 (1936).

³¹³ Blum, I., *Bul. Chim. Soc. România Stiinte*, 31, 3-11 (1931).

³¹⁴ Krym, V. S., *Fuel*, 6, 476-8 (1927).

CLASSIFICATION IN OTHER COUNTRIES

and coking property need to be specified. Anthracite and other noncoking coals were classified according to size. Stadnikoff³¹⁵ presented a tentative commercial classification of Russian coals, and Matyushenko²⁵² used many chemical and physical tests, including a special burning test on grates to determine reactivity, degree of deformation of coal under heat, and resistance to thermal shock. He presented a large table classifying coals from lignite to anthracite, based on 2,200 coals tested.

Evans³¹⁶ discussed the classification of New Zealand coals according to type or petrographic constituents, rank, cleavage, analysis, coking properties, etc.

In addition to the previously mentioned

³¹⁵ Stadnikoff, G. L., *Khim. Tverdogo Topliva*, **4**, 513-27 (1933).

³¹⁶ Evans, W. P., *New Zealand J. Sci. Tech.*, **7**, 79-90, 155-70, 198-215 (1924).

studies by Wong¹²⁰ and Wang,¹²¹ a graphical classification of Chinese coals has been made by King.³¹⁷

CONCLUSION

The scope of coal classification is so great that it has not been practical to include comprehensive bibliographies on the many subjects discussed. By consulting the originals of the articles cited above, many additional references can readily be obtained on any subject in which the reader is particularly interested.

An attempt has been made in the foregoing chapter to give some attention to almost every phase of the subject and to show that there are as many methods of coal classification as there are viewpoints concerning the nature and uses of coal.

³¹⁷ King, K. Y., *Bull. Geol. Surv. China*, No. 21, pp. 1-11, 1933.

CHAPTER 3

COAL PETROGRAPHY *

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Coal petrography has been maintained as a branch of science since 1920 because a number of geologists have accepted the petrographic point of view enunciated by Stopes as suitable for the description and classification of coal and have directed inquiries toward discovering the practical significance of the data. Along with the development of a technique and a nomenclature of coal petrography there has been advancement in the understanding of the botanical significance of the petrographic entities. This development is indicative of the newer attitude toward coal material. A portion of the coal, such, for example, as the opaque matter in splint coal, may be recognized as a petrographic component whether or not its nature is understood. On the other hand, the importance of understanding the nature of the material represented by the petrographic constituents calls for persistent and careful paleobotanical studies bearing on the nature of these materials. More and more the study of coal balls, for example, is being directed toward the discovery of the actual nature of the materials present in the coal as seen in maceration residues, in thin sections, or in polished surfaces.

As in preceding years, the development of knowledge and the technical discussions

in the fourth decade of the century were very largely centered about three main schools of thought, the continental European, the British, and the American. The discussion will, therefore, necessarily have to take into consideration the regional attitude toward coal petrography.

DESCRIPTION AND TERMINOLOGY IN RECENT COAL PETROGRAPHY

By 1920, geologists and others interested in the physical constitution of coal, considered as a rock material, had been provided with two fundamental schemes of coal nomenclature as a basis for petrographic studies and description. That proposed by Thiessen was primarily genetic, being based upon the kind of plant material composing the various parts of the coal that could be differentiated. Its criteria were microscopic and paleobotanical. The nomenclature of Stopes, on the other hand, was based upon physical megascopic differences apparent without microscopic aid. The terminology proposed by Thiessen was of somewhat uncertain and difficult application to hand specimens and by definition permitted inclusion in anthraxylon as "coalified wood" of such diverse material as the bright banded vitrain and fusain, and in attritus of both fine banded bright coal (clarain) and splint (durain). It was not a classification well suited to

* Presented with the consent of M. M. Leighton, Chief, Illinois State Geological Survey.

megascopic application. On the other hand, the Stopes nomenclature which was applicable to the hand specimen consisted of rather happily selected new names similar to the single name in use, *fussain*. The terminology was essentially such as to include all the more important, at least the more conspicuous, of the varieties of coal present in banded coal, with relatively little overlapping, except that transitional varieties were recognized. It is not strange that the possibilities of a simple systematic description and classification of coal provided by the Stopes nomenclature were very widely recognized in Europe, where no opposing influential agency supported an alternative system of nomenclature. We find, therefore, in the literature since 1920 many discussions of the Stopes terminology.¹

1 Thiessen, R., *Coal Age*, 18, 1183-9, 1223-8, 1275-9 (1920), 19, 12-5 (1921); *Trans. Am. Inst. Mining Met. Engrs.*, 71, 35-116 (1925); *Colliery Guardian*, 131, 743-4 (1926); *J. Roy. Soc. Arts*, 74, 535-55 (1926). Baranow, A., and Francis, W., *Fuel*, 1, 219-22 (1922). Findley, A. E., and Wiggington, R., *Fuel*, 1, 106-7 (1922). Stopes, M. C., *Fuel*, 1, 22-5 (1922), 2, 5-9 (1923). Seyler, C. A., *Fuel*, 2, 217-9 (1923); *Dept. Sci. Ind. Research (Brit.)*, *Fuel Research Board, Phys. Chem. Surv. National Coal Resources*, 16, 32-8 (1929). Stutzer, O., *Kohle (Allgemeine Kohlengologie)*, Gebrüder Borntraeger, Berlin, 1923, pp. 58-61. Winter, H., *Glückauf*, 59, 873-80 (1923), 63, 483-91 (1927); *Fuel*, 3, 134-9 (1924), 7, 56-63 (1928). Duparque, A., *Ann. soc. géol. Nord*, 49, 148-59 (1924), 52, 261-72, 273-9 (1927). Gothan, W., *Tech. Blätter*, 15, 377-8 (1925). Hendrickson, A. V., *Fuel*, 4, 83-6 (1925). Simpkin, S. N., *Colliery Guardian*, 129, 515 (1925). Stach, E., *Glückauf*, 61, 1398-402 (1925); *Kohlenpetrographisches Praktikum*, Gebrüder Borntraeger, Berlin, 1928, pp. 89-126. Turner, H. G., and Randall, H. R., *Trans. Am. Inst. Mining Met. Engrs.*, 71, 127-48 (1925). De Booseré, O., *Ann. mines Belg.*, 27, 369-96 (1926); *Fuel*, 5, 522-7 (1926). Bode, H., *Kohle u. Erz*, Jahrg. 1927, pp. 793-802 (1927), Jahrg. 1928, pp. 699-710 (1928); *Z. deut. geol. Ges.*, 81, 151-5 (1929). Kellett, J. G., *Trans. Inst. Mining Engrs. (London)*, 75, 400-12 (1928); *Colliery Guardian*, 137, 240-2 (1928). Legraye, M., *Ann. soc. géol. Belg.*, 51B, 316-7 (1928), 52B, 100-2 (1929). Po-

During this period, two main fields of controversy in regard to terminology had developed. On the one hand, attempts were made to correlate the Stopes terminology with that proposed by Thiessen; on the other hand; there developed in Europe a tendency toward a revision of the Stopes classification on the basis of primary criteria which were microscopic rather than megascopic.

In respect to the terminologies of Stopes and Thiessen, uncertainty existed concerning the significance of one set of names in the terms of the other terminology. The status of the controversy near the end of the third decade was summarized by Thiessen and Francis in 1929.² In this paper the authors pointed out that the two sets of terms were evolved in different manners. In regard to the origin of "anthraxylon" and "atritus," they said:

Instead of describing the different bands of coal from their appearance, the terms were made to suggest the origin of the different types of material that the coal contains. Moreover, the investigations which led to their conception were confined to American coals, not of one geologic age or necessarily of one rank. They were, in fact, suggested as a result of microscopic examination showing that throughout a complete series of coals, beginning with peat (if, indeed, peat may be called coal) and terminating with semibutuminous coal and anthracite, two main types of materials persisted.

These writers had already pointed out³ "that the terms proposed by Stopes were specifically stated to apply only to British Paleozoic coal of Bituminous rank." This statement is not exactly correct, as Stopes

tonié, R., *Jahrb. preuss. geol. Landesanstalt*, 48, 128-30 (1928). Thiessen, R., and Francis, W., *U. S. Bur. Mines, Tech. Paper*, 446 (1929), 27 pp.; *Fuel*, 8, 385-405 (1929).

² Thiessen, R., and Francis, W., *U. S. Bur. Mines, Tech. Paper* 446, 3 (1929).

³ See p. 1 of ref. 2.

did not say that the terms were not applicable to other coals, but that "the coal dealt with is British Paleozoic (Coal Measure) streaky bituminous coal." The applicability of these terms to other coals might or might not have been discussed by Stopes but would eventually be determined one way or another. Events have proved the wide applicability of the terms to all coal material, at least to that above lignite in rank.

The summary of the discussion of the correlation of terms as given by Thiessen and Francis reads as follows: ⁴

The two recent attempts to distinguish the various types of coal (Paleozoic) present in any bed may be correlated as follows:

Vitrain, the same as *anthraxylon*. Brilliant bands with conchoidal fracture.

Clarain, the same as *atritus*. The thin bright streaks in clarain are bright streaks of vitrain (anthraxylon), which can be readily separated from the duller portions. Inherently laminated, it breaks sharply with a smooth surface at the break.

Durain. A dull-band granular coal; it has no counterpart in America [*sic*]. It is difficult to break, and the surfaces are always granular or matte. It is composed of opaque matter and spores in varying proportions.

Fusain. Present universally in small quantities, dark fibrous, and powdery; it corresponds to the mineral-charcoal or mother-of-coal in America.

The authors then stated that "the terms 'anthraxylon,' 'atritus,' and 'fusain' may be used irrespective of rank or geological age of the coal, whereas the terms 'vitrain,' 'clarain,' and 'durain' should only be used for coals of bituminous rank," a conclusion that is untenable, because the fact that only British coals were used in developing the terms does not limit their applicability, as has been abundantly demonstrated by their widespread use. However, such statements by Thiessen and his

associates, who had an overwhelming influence in the early development of the technique of coal petrography in America, resulted in an important bias against the general use of the British terms on this continent.

The statement made by Thiessen in 1929 that there was no counterpart of durain in America was shortly after offset by his description of splint coal ⁵ and by the differentiation of "opaque" and "translucent attritus."

In 1931, the Bureau of Mines described the methods used in the study of gas-, coke-, and byproduct-making properties of representative American coals.⁶ In connection with this study, Thiessen inaugurated a "type" classification of banded bituminous coal based upon the proportion of microscopically determined anthraxylon and opaque and translucent attritus, the anthraxylon being differentiated on the basis of the width of individual bands. The classification adopted was presented in the following words: ⁷

Up to the present no one has laid down any definite system for classifying coal on the basis of the relative percentage of anthraxylon and attritus, as determined by actual measurement with the aid of the microscope. Such a system of classification is desirable in the present investigation because of the difference in the coking properties of anthraxylon and attritus. It has been decided, therefore, to make arbitrary division of classification as follows:

⁵ Thiessen, R., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 644-72 (1930).

⁶ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **344** (1931), 107 pp.

⁷ See p. 24 of ref. 6.

⁴ See p. 26 of ref. 2.

CLASSIFICATION OF SUBTYPES OF COAL ON THE BASIS OF ANTHRAXYLON-ATTRITUS RATIO

Type Name	Abbreviation	Ratio of Anthraxylon to Attritus
Anthraxylon	An	More than 3 : 1
Anthraxylous-attrital	An-At	3 : 1 to 1 : 1
Attrital-anthraxylous	At-An	1 : 1 to 1 : 3
Attrital	At	Less than 1 : 3

The adjectives are so employed in the table as to result in confusion in regard to the meaning of the terms.

The banded structure was designated under four categories:⁸ coarsely banded, bands exceeding 2 millimeters; finely banded or striped, bands from 2.0 to 0.5 millimeters; microbanded, less than 0.5 millimeter. A mixed banded coal contains both coarse and fine bands. Anthraxylon was subdivided into ordinary and fibrous

anthraxylon, the fibrous consisting of thin, fiberlike strands down to 0.05 millimeter thick.⁹

Thiessen also presented a table⁸ proposing definitions of the common types of coal in terms of attritus and anthraxylon (see Table I).

In accordance with the classification by the U. S. Bureau of Mines, Thiessen, Sprunk, and O'Donnell, or Sprunk and O'Donnell, up to the end of 1939 had described about 30 American coals in connection with the study of coke-, gas-, and by-product-making properties of the coals. The classification was made in terms of what Thiessen calls types (bright or humic, semisplint, splint, cannel, and boghead coal) and subtypes (anthraxylous, anthraxylous-attrital, attrital-anthraxylous, and attrital coal), and with respect to the pro-

⁸ See p. 25 of ref. 6.

⁹ See pp. 63 and 69 of ref. 6.

TABLE I

THIESSEN'S DESCRIPTION OF TYPES OF COAL⁸

Type Name of Coal	Relative Amounts of Anthraxylon and Attritus	Nature of Attritus	Structure of Coal
Bright	Anthraxylon predominating to attritus predominating	Translucent humic matter predominating. Spores and opaque matter present.	Coarsely, finely, or microbanded. Bright luster.
Semisplint	Anthraxylon and attritus in more or less equal proportions	Granular opaque matter very prominent. Opaque and translucent humic matter present.	Finely or microbanded. Compact.
Splint	Attritus predominating	Opaque matter predominating. Spores and translucent matter present.	Finely or microbanded. Compact, hard, irregular fracture. Dull luster.
Cannel	Almost all attritus	Spores, humic matter, or opaque matter predominating.	Compact, not banded, conchoidal fracture.
Boghead	Almost all attritus	Oil algae predominating. Humic and opaque matter present.	Compact, not banded, conchoidal fracture.

portions of the components (anthraxylon, fibrous anthraxylon, translucent or opaque attritus, and fusain). Classification of the different coals was based upon the microscopic identification of the components.¹⁰ Bright coal may be anthraxylous or anthraxylous-attrital; splint coals are attrital. Semisplint coals may be anthraxylous-attrital or attrital-anthraxylous, depending upon whether the anthraxylon or opaque attritus predominates. Cannel and boghead are regarded as attrital coals.

Thiessen¹¹ has classified coals in the categories of "coals composed of both anthraxylon and attritus," and "coals composed of attritus," and he arranges "types of coal" under the headings "banded coals" and "cannel coals" as follows:¹²

Banded coals.

- (a) Anthraxylous coals.
- (b) Anthraxylous and attrital coals in more equal proportions.
- (c) Attrital coals.
- (d) Splint coals (opaque attrital).
- (e) Humic coals (lucid attrital).
- (f) Spore coals.
- (g) Humic-spore and spore-humic coals.

Cannel coals.

- (a) Spore-cannel coals.
- (b) Pseudo- or humic-cannel coals.
- (c) Boghead or algal-cannel coals.
- (d) Spore-humic cannel coals.
- (e) Spore-opaque-attrital cannel coals.
- (f) Spore-boghead coals.

Banded coals have a banded structure due to the presence of anthraxylon lenses. These may be numerous, as is characteristic of common-banded coals, or only few as is characteristic of splint coals. The in-

tervening attrital material may be composed of various materials either in fairly concentrated state or mixed in various proportions. Thiessen recognized several varieties or types of attritus or attrital coals:¹³ (a) humic coals, (b) spore coal, (c) resinous coal, (d) paper coal, and (e) splint coal. "Splint coals," stated Thiessen, "are quite different from other coals and are easily distinguishable from them, particularly in thin sections under the microscope." (Figure 1.) "They are irregular and lumpy, irregular or rough in fracture, grayish black in color, and of granular consistency." (Figure 2.)

In a more recent publication, Thiessen¹⁴ modified earlier classifications and recognized "banded coals" and "nonbanded coals." Three classes of banded coals were set up: "bright coals," "semisplint coals," and "splint coal." Bright coals were subdivided into subtypes on the basis of the proportion of anthraxylon and attritus present (see page 89) and might also be classified "by virtue of the predominance of the constituent" into (1) typical bright banded coals, (2) spore-rich coals, (3) resinous coals, (4) coals rich in cuticle ("paper coals"), (5) leaf coals and coals composed largely of bark. In spore-rich, resinous, cuticular, and leaf coal, the diagnostic component makes up more or less of the attritus. The bark, however, is generally represented by anthraxylon, and anthraxylon may also be very resinous.

Splint coal was defined by Thiessen¹³ as one composed of anthraxylon and attritus, of which the latter, consisting of brown cell wall degradation matter and granular opaque matter, forms the larger part.

¹³ See p. 64 (1930) and p. 123 (1931) of ref. 11.

¹⁴ Thiessen, R., *Proc. Fuel Engrg. Conf., Fuel Engrg. Div., Appalachian Coals, Inc.*, 4, 211-72 (1937).

¹⁰ See p. 31 of ref. 6.

¹¹ Thiessen, R., *Illinois State Geol. Survey, Coop. Mining Series Bull.* 33, 58-89, especially 63-66 (1930); *Illinois State Geol. Survey, Bull.* 60, 117-31 (1931).

¹² See p. 66 (1930) and p. 124 (1931) of ref. 11.



FIG. 1. Thin cross section of splint coal from the High Splint Seam, Harlan County, Kentucky. The ground mass consists of opaque matter and in a medium thin section is entirely opaque, only the spores, occasionally resin particles, and strips of humic matter being transparent.¹¹ ($\times 200$.)

Translucent humic matter, resins, and finely divided fusain are present in smaller proportions, and spores in greatly varying proportions.

Semi-splint coal... is one in which the proportions of anthraxylon and attritus are

tween bright coal and a splint, in other respects, it has characteristics of its own.

Coal petrography as advanced by Thiesen recognizes the existence of a variety of coals. Variation, however, is interpreted

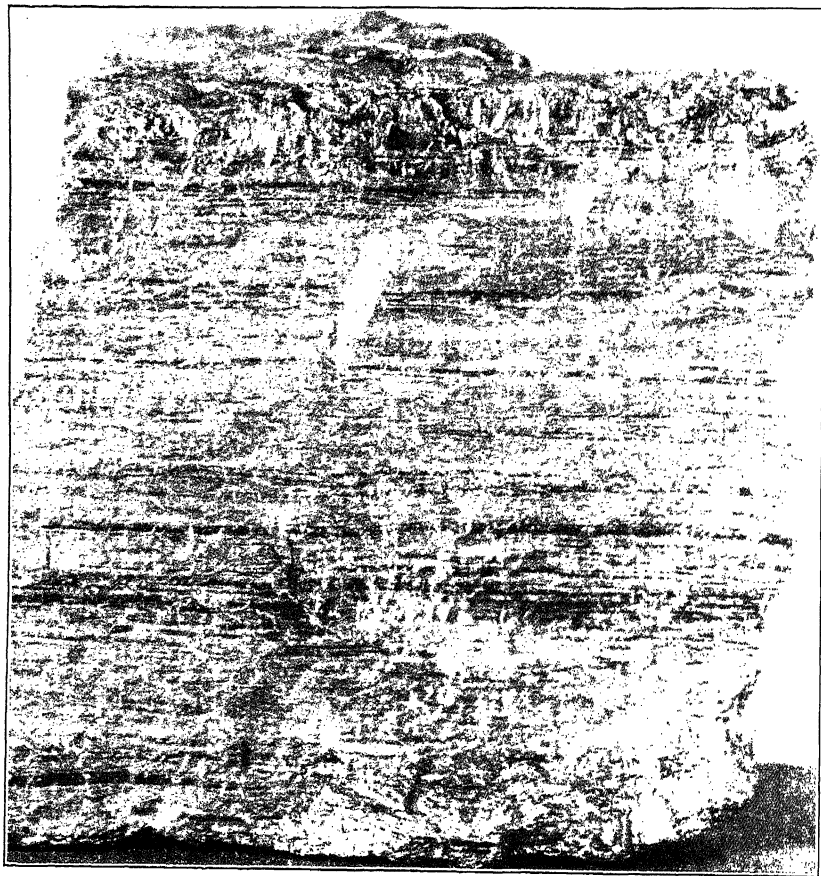


FIG. 2. A block of splint coal from the High Splint Seam, Closplint Mine, Harlan County, Kentucky. Characteristics of the splint coals are the large number of relatively thin anthraxylon sheets and the relatively great amount of attritus. The attritus in this coal is composed largely of opaque matter, spores, and some humic and resin matters.¹⁵ (Slightly less than natural size.)

more or less equal, but of which the attritus is essentially composed of brown and granular opaque matters in varying proportions. Translucent humic matter, spores, pollens, and finely divided fusain are always present in small proportions. In certain respects its composition is medium be-

as an effect of variation in the initial plant material or in the residual plant material after more or less decomposition in the peat swamp.¹⁵ It is assumed that the fos-

¹⁵ Thiesen, R., and Sprunk, G. G., *Fuel*, 15, 304-15 (1936).

sil plant components of the coal represent, in their form as coal, differences qualitatively the same as those differences which the plant parts or secretions possessed in the living state, or at least in their undecayed and otherwise unmodified state. Hence it appears logical to classify coals on the basis of their initial constitution and to call the varieties of coal thus set up petrographic varieties, a conclusion that is not universally accepted.

The development of the European system of nomenclature for coal petrography is based upon the classification of the "coal ingredients" set up by Stopes.¹⁶ This system of nomenclature has suffered greatly in its usefulness because of diverse interpretations that have been placed upon Stopes's original inadequate and unsatisfactory definitions. This is undoubtedly one of the important reasons for the unwillingness of Thiessen to adopt the British terminology. The history of the changes in nomenclature between 1919 and 1935 have been well summarized by Roos,¹⁷ who first called attention to three sources of confusion in the use of the Stopes terminology: microscopic criteria have served as a basis for the differentiation of ingredients set up on the basis of macroscopic criteria; the terminology is not definitely applicable to coals with less than 20 percent volatile matter because of diminution of contrasts in the luster of the ingredients; and ingredients originally regarded as structureless have since been found to possess structure. According to Roos several authors have misused the word vitrain. He quoted a discussion by

Stopes of an article by Hickling and Marshall¹⁸ in which she wrote:

I do, however, deplore and enter an explicit protest against the misuse of the word vitrain. Vitrain was defined as being a structureless jelly; any bright coal in which tissue is preserved, and not decomposed into a complete jelly, cannot be vitrain. It confuses the whole science involved in coal research.

Although this interpretation placed upon the meaning of the term vitrain did little but confuse the application of this name, Roos stated that "the greatest difficulty was caused by the terms clarain and durain." The interpretation by European geologists of the description by Stopes of these ingredients is expressed in the following quotation from Roos:¹⁹

Clarain comprised after the definition of Stopes the following types of coal:

1. Coal having no discrete plant entities, but showing any structure (also the obliterated structure, which can only be detected after etching of the polished surface of the coal preparation or by other methods).

2. The translucent gel, mixed with spores, cuticles, etc., in the most widely different quantities.

In contrast to this opinion, other authors have considered the relative quantities of the colloidal binding material and the resistant structures plant entities as characteristic of clarain. So W. Francis²⁰ defines clarain as containing a small percentage, usually not more than 5 percent, of resistant plant remains, such as spore exines and cuticles. Coal with more of these remainders is classified by Francis as durain.

There appeared a tendency to regard clarain as merely a mixture of vitrain and durain. As stated by Roos,²¹ Hickling²²

¹⁸ Hickling, H. G. A., and Marshall, C. E., *Trans. Inst. Mining Engrs. (London)*, **86**, 56-85, especially 79 (1933).

¹⁹ See p. 1074 of ref. 17.

²⁰ Francis, W., *Fuel*, **11**, 171-6 (1932).

²¹ See p. 1075 of ref. 17.

²² Hickling, H. G. A., *Fuel*, **10**, 212-32 (1931); *Proc. S. Wales Inst. Engrs.*, **46**, 911-51 (1931).

¹⁶ Stopes, Marie C., *Proc. Roy. Soc. (London)*, **90B**, 470-87 (1919).

¹⁷ Roos, G., *Compt. rend. deuxième congr. l'avance. études strat. Carbonifère, Heerlen, 1935*, **3**, 1074-7 (1937).

in 1931 said that "the term clarain covers a wide variety of coal types, from those which are nearly pure vitrain, to those in which the proportion of vitrain is so small that it ceases to differentiate the mass from the typical durain." Jongmans and Koopmans²³ have declared that clarain is a mixture of telain (vitrain showing plant structure) and durain, and accordingly the term clarain is not used by the Netherlands Geological Bureau.

Hoffmann²⁴ has stated that in Germany for some time the alleged similarity of clarain and durain caused abandonment of use of the term clarain (*Clarit*), coals being described in terms of vitrain (*Vitrit*), durain (*Durit*), and fusain (*Fusit*). Kühlwein²⁵ by 1935 had revived the term clarain (*Clarit*), and the four terms proposed by Stopes were in use by the coal petrography laboratory at Bochum.

The development of coal-petrography nomenclature in France, Belgium, and Holland is described in the following summary by Roos:²⁶

A. Duparque²⁷ studied polished surfaces of coal in reflected light, without etching them. He began by adopting the nomenclature of Stopes, using the names vitrain [the fundamental substance forming the entire mass of the constituent], clarain [fundamental substance dominant, but containing some debris and sclerenchyma; spores and algae somewhat uncommon], durain [numerous large and small spores; somewhat infrequent fragments of wood and sclerenchyma; fundamental substance little developed], and fusain.

²³ Jongmans, W. J., and Koopmans, R. G., *Geol. Bur., Heerlen, Yearbook 1933*, pp. 49-63 (1934).

²⁴ Hoffmann, E., *Compt. rend. deuxième congr. l'avance. études strat. Carbonifère, Heerlen, 1935*, 1, 313-25, especially 318 (1937).

²⁵ Kühlwein, F. L., *ibid.*, 2, 539-601 (1937).

²⁶ See pp. 1076-9 of ref. 17.

²⁷ Duparque, A., *Compt. rend. congr. soc. savantes Paris et dept. Poitiers, 1926*, 227-35 (1927).

Shortly afterwards he proposed the names xylain and xylovitrain:

Xylain [lignified tissues transformed into brilliant coal owing to a partial jellying, but displaying structure clearly visible under the microscope comparable in every way to the cellular structure of fusain].

Xylovitrain [lignified tissues transformed into brilliant coal but having undergone complete jellying (transformation into an amorphous material). The aspect of the material is identical to that of vitrain, but the distribution and form of the contraction voids differentiate it clearly].

Vitrain [vitrain, which is formed solely by the precipitation of the fundamental substance, does not contain traces of lignified tissue].²⁸

In 1927,²⁹ he gave another classification, with new names: *houille matte*—durain (Stopes), *houille semibrillante*—clarain (Stopes), *houille brillante*—vitrain (Stopes).

Roos also summarized the classification proposed by Legraye,³⁰ based upon the examination of polished coal surfaces, stating that the following varieties were distinguished:

bright coal or vitrain—coal without apparent structure; dull coal or durain—composed of debris which are embedded in vitrain; clarain—all intermediates between vitrain and durain; and fusain.

The fact that the coal, particularly when examined by incident light as polished surfaces, appeared to contain vitrainlike material, some of which showed discernible cell structure and some of which appeared to be structureless, appeared to some investigators to require some recognition in classification and nomenclature. Hence Jongmans and Koopmans³¹ differentiated the following materials:

²⁸ Duparque, A., *Ann. soc. géol. Nord*, 51, 51-64 (1926).

²⁹ Duparque, A., *ibid.*, 52, 273-96 (1927).

³⁰ Legraye, M., *Rev. universelle mines*, [8] 7, 191-6 (1932).

³¹ See pp. 49-63, especially p. 50, of ref. 23.

Vitrain (*Vitrit*): Completely structureless groundmass by which the coal is permeated and which serves as a binding material.

Durain (*Durit*): Micro conglomerate of small coal fragments which are embedded in the groundmass of vitrain.

Telain (*Telit*): Large cell fragments permeated by vitrain, which material fills the cell spaces.

Fusain (*Fusit*): Cellular fragments not permeated by vitrain and with a charcoal-like appearance.

Transition types of coal were recognized and given such names as vitrofusain, telofusain, durovitrain, telovitrain, fusovitrain, telodurain, fusodurain, durotelain, vitrotelain, and fusotelain, the meaning of each of which is fairly self-evident.

In January, 1935, Stopes³² presented (see Table II) a classification of coal ingredients in which she revised and expanded her original ideas presented in 1919,¹⁶ among other suggestions proposing that the coalified plant materials, or products of the disintegration of plant materials, represented in the coal be regarded as equivalent to minerals in their relation to the composition of coal as a whole. For these components of coal she devised the name *macerals*, suggested by the name mineral. She also revised her original definitions of the banded ingredients, which she now included under the general group of "rock types." The meaning of vitrain was expanded to include, without question, the brilliant glossy bands that showed cell structure under the microscope.

However, the existence of structureless vitrain was insisted upon, and coal or vitrain consisting of this kind of material was named eu-vitrain, the vitrain showing structure being named pro-vitrain. The eu-vitrain was further subdivided into *ulmain*, described as "completely jellified plant material which may, for example, lie

at one end of only partly jellified stem," and *collain*, described as "redeposited ulmin compounds precipitated from solution." Presumably this is the translucent structureless material which can be seen in thin sections of coal filling the cell spaces, and also possibly represents what Duparque²⁸ and Potonié³³ designated as "redeposited gel." No important changes were made in the definitions of clarain, durain, or fusain.

The microscopic appearance of the rock-type varieties was described in considerable detail (Table II). In this description, the macerals constitute "the organic units composing the coal mass . . . and are the descriptive equivalent of the inorganic units composing most rock masses and universally called minerals."

In regard to the identification of macerals, Stopes stated that "they are only visible when thin sections are prepared for the microscope, or sometimes, when polished surfaces are examined under high-powered lenses before or after specific etching treatment."

The schedule of nomenclature was built up from the following outline:

ROCK TYPES		MACERALS	
Lithological Name of Hand Specimen		(Petrographic Units, Microscopic)	
Simple	Vitrain	Vitrinite	
		Fusinite	
Complex	Clarain	Vitrinite	
		Xylinite	
		Exinite, etc.	
	Durain	Micronite (residuum)	
		Exinite	
		Cutinite, etc.	

The system of nomenclature for the macerals devised by Stopes requires, in a

³² Stopes, Marie C., *Fuel*, 14, 4-13 (1935).

³³ Potonié, R., *Deut. geol. Ges.*, 78, 348-80 (1926).

TABLE II
A CLASSIFICATION BY STORES OF COAL INGREDIENTS ^{3,2}

Lithological classification of hand specimens of coal as a rock (Rock Types)		Microscopic data and petrological units (MACERALS)	
Megaoscopic appearance of hand specimens.	Lithological name of hand specimens.	Constituent petrological units (new name MACERALS minerals in crystalline rocks).	
		General appearance in microscopic sections (exceptions possible).	Original nature (in brief, simple terms).
Thin horizontal bands visible to naked eye up to 20 mm thick, though may be in thicker lenses. Brilliant gloss, vitreous, strong rectangular fracture perpendicular to bedding, conchoidal fracture in other directions. Clean specular reflection. Very friable into small cubes with curved sides; quite clean to the touch. Not intrinsically stratified parallel to the bedding plane, but may show striations due to plant structure irrespective of bedding plane.	A Vitrain § En-Vitrain (structureless)	Ulmun (completely jellified plant material, e.g., lie at one end of only partly jellified stem)	Ulmunite
		Collun (re-deposited ulmin compounds precipitated from solution)	Collunite
		Peribain (where its cortical origin is evident) _{as}	Peribainite
		Subrain (where its corky origin is evident)	Subrainite
		Xylun + (where its woody origin is evident)	Xylunite Resinite
		Pro-Vitrain * (ghostly or distinctly indicated structure)	Pro-Vitrainite
			En-Vitrainite
			Vitrite
			Fusinite
Irregular wedges lying on bedding planes at various angles. Fibrous appearance with sheen on individual fibers in dull opaque texture depending on incidence of light. Very friable, breaking down to a soiling black powder. Resembles charcoal in appearance.	B Fusain		

Xyinite Perlibnite Suberinite Collinite Resinite + Ulminite Cufinite Exinite Fusinite + Sometimes Micronite ("Residuum")	Distinctive	Clarinite †

All parts of any plant may contribute to the irregularly sized composite leucite of tissue; structureless ulmin may be present.

Striated appearance due to fragments of plant tissues in various stages of disintegration in semi-translucent translucent zones with zones cuticle structureless in addition to recognizable intercalated zones of vitrinite. Golden to amber-red, cuticles, spores, resin bodies. Lenticels of tissue in condition of Fusain not infrequent.

C Clarain

Thin or very thick bands, intrinsically stratified parallel with the bedding plane. Breaking irregularly to bedding plane most often with silky or satin gloss or diffuse reflection markedly less intense than the specular reflection of Vitrain under the same illumination. No conchoidal fracture, but splits in sheets or rectangular direction. Less friable than A.

Micronite ("Residuum") Exinite Cufinite Resinite + Collinite Xylinite Suberinite Ulminite Fusinite	Distinctive	Durinite †

The matrix of minutely macerated fragments may be resolved generally, but even in thinnest sections leaves a *Residuum*, often opaque. All parts of any plants may contribute but (with a few exceptions) spores are the most conspicuous resistant remains and the minutely fragmented nature of all else is characteristic.

Very fine granular ground mass, often semi-opaque even in very thin sections. In the finely comminuted material spore exines, when present, are generally (though not always) conspicuous. Thick golden and orange walls of macrospores compressed parallel to bedding plane. Some or many macrospores in finely comminuted cuticular and other fragments. Resin bodies and larger cuticles may be locally dominating. Very variable. Black cubic crystals of iron sulfide often present.

D Durain

Solids bands may be thick or thin, hard with a edges from texture, surface broken finely granular and irregular. Appearance matte even in thin sections. Compact heavy texture. Stratification generally absent but may be obvious in some American coals, less so in European types.

* Pro-Vitrain may or may not show to the naked eye a striation which depends on its cellular structure and is not intrinsic stratification parallel to the bedding plane and which may be horizontally compressed parallel to the bedding plane or may be irregular.

† "Anthraxylon," as used in some of Theissen's papers, includes Suberinite as well as Ulmin, so is not the exact equivalent of any one of these. Mainly it tallies with Pro-Vitrain.

‡ For repetitive description the terms *Clarinite* and *Durinite* may be used although they are not individual minerals and therefore not strictly equivalent to *Vitrinite* or *Fusinite*.

§ The five subdivisions of Vitrain will not always be determined by means of present technique, though all have been identified.

A, B, C, and D may contain any or all of the minerals: chiefly, iron pyrites, hydrated aluminium silicates ("clays"), silica, carbonates (various), also free hydrocarbons, gas inclusions, sorbed gas, water.

COAL PETROGRAPHY

general way, that each recognizable plant tissue, organ or secretion, be given a distinct name as representing a distinct substance. Thus corky tissue in vitrain is called *suberinite*, material thought to be resin, *resinite*; exine material, *exinite*; cuticular material, *cutinite*; particles of fusain or the material of which fusain is composed, *fusinite*; etc. This nomenclature divorces substance from form, although it is doubtful whether, as materials occur in coal, substance is possible of identification divorced from form, or that it ever occurs divorced from form except possibly for the resins and isolated waxy bodies.

Those to whom such a system of nomenclature is proposed must judge whether or not it is more effective to state that a coal contains numerous exines, for example, than to say that it contains considerable scattered exinite, when, in order to complete the picture, it is necessary to add that the exinite occurs in the form of scattered fossil exines. To some, at least, the nomenclature is an unnecessary elaboration of the academic conception of an analogy between coal and rock and coal components and rock minerals. Irrespective of the merits and usefulness of the term "maceral" the writer believes that convenience would be served if all fossil vegetative forms in coal were designated "phyterals" (Φυτὸν Greek meaning plant, *eral* as in mineral), the phyterals having somewhat the same relation to macerals as crystals to minerals.

The European system of nomenclature was summarized in the deliberations of the Second Congress of Carboniferous Stratigraphy at Heerlen in 1935, as reported by Jongmans, Koopmans, and Roos.³⁴ The schedule of names and clas-

sification in Table III was agreed upon by all members of the round-table conference represented by members from England, Germany, Austria, and Holland. A

TABLE III

SCHEDULE OF COAL NOMENCLATURE ADOPTED
BY THE HEERLEN, 1935, ROUND TABLE

<i>Kohlenarten</i>	Rock Types <i>Streifenarten</i>	Macerals <i>Gefügebestandteile</i> (<i>Mazeralien</i>)
<i>Gasflammkohle</i> , etc.	1. Fusite (Fusain)	1. Fusinite
	2. Vitrite (Vitrain)	2. Semifusinite
	3. Clarite (Clarain)	3. Vitrinite { Collinite Telinite
		4. Resinite
		5. Exinite
		6. Micronite (Opaque substance)
	4. Durite (Durain)	

memorandum on the proceedings of the conference prepared by Seyler which is included in the article by Jongmans, Koopmans, and Roos contained the following statements:

For the rock types (German equivalent: *Streifenarten*) the terms vitrite, clarite, durite were adopted (these being spelled Vitrit, Fusit, etc., in German). The long-established termination *-ain* was retained for the rock types in English and French. For the micro-petrological units, Dr. Stopes' term "macerals" (or an equivalent form such as the German *Mazeralien*) was accepted with an alternative *Gefügebestandteile* in German.

In the main, the names proposed by Dr. Stopes for the macerals were accepted. It was, however, preferred to use the names collinite and telinite (instead of eu-vitrinite and pro-vitrinite) for vitrinite respectively devoid of structure and showing structure on polishing, etching, or thin sectioning. Further distinctions of telinite according to botanical origin such as xylinite, periblinite, suberinite, were accepted, but were considered unnecessary for general use. In the

Roos, G., *Compt. rend. deuxième congr. l'avance. études strat. Carbonifère, Heerlen, 1935*, 3, 1733-5 (1938). See also Kukuk, P., and Kühlwein, F. L., *Glückauf*, 71, 1275 (1935).

³⁴ Jongmans, W. J., Koopmans, R. G., and

same way, the name ulminite was approved for vitrinite devoid of structure.

Fusinite was retained for the chief maceral of fusite.

It was thought necessary, however, to introduce a term semifusinite (German: *Halbfusinit*) for material intermediate between vitrinite and fusinite.

The term resinite for constituents resembling resin was accepted.

The term exinite was adopted for the material of spore exines and cuticles. To dis-

Hoffmann²⁴ in 1935 summarized the nomenclature of coal petrography for what are called the "coal types" in the Heerlen Congress as shown in Table IV.

Raistrick and Marshall³⁵ in 1935 presented a type classification in which the European terminology was adopted (Tables V and VI) with the introduction of some novel ideas, and in which consideration was given to the interpretation

TABLE IV
COMPARISON OF THE NOMENCLATURE FOR COAL TYPES (BANDED INGREDIENTS) AS APPLIED IN DIFFERENT COUNTRIES²⁴

Macerals	Germany	England		U. S. A.		France	Belgium	Holland
<i>Fusit</i>	<i>Faserkohle</i>	Mineral charcoal	Fusain	Mineral charcoal		<i>Fusain</i>	<i>Fusain</i>	<i>Fusit</i>
<i>Telit</i>	<i>Glanz-kohle</i>	Bright coal	Vitrain	Bright coal	Anthraxylon	<i>Houille brillante</i>	<i>Charbon brillant</i>	<i>Telit</i>
<i>Vitrit</i>								<i>Vitrit</i>
<i>Clarit</i>			Clarain	Semi-splint	Trans-lucent attritus	<i>Houille semi-brillante</i>	<i>Charbon semi-brillant</i>	<i>Durit</i>
<i>Durit</i>	<i>Mattkohle</i>	Dull coal	Durain	Splint	Opaque attritus	<i>Houille matte</i>	<i>Charbon mat</i>	

tinguish cuticular material and spore-exines, the terms cutinite and sporinite were approved, although it was the opinion of the conference that this distinction is not usually necessary. "Exinite" would then correspond to the "resistant plant material" of Wheeler's "rational analysis" (with the exception of fragments of fusinite).

The term micronite for the opaque "residuum" of durite was adopted in the form "micrinite" in order to keep to the ending *-inite* for macerals. This is philologically permissible since it is formed from "micronite" by the elision of the "o" before the suffix *-inite*.

It was agreed that, in addition to the rock types vitrain (*Vitrit*) and fusain (*Fusit*) both the terms clarain (*Clarit*) and durain (*Durit*) must be retained, clarain consisting mainly of vitrinite admixed with exinite, and durain of micrinite admixed with exinite.

of American terminology in European terms. Their type classification was based on an understanding that "type is determined by the kind of plant material from which the coal is formed and is therefore an inherent characteristic of the coal." Major categories of coal types were distinguished, these categories being textural and not botanical, as would seem to be required if the classification is to be in line with the main basis of classification. However, the primary categories proposed were dependent upon the size of grain,

³⁵ Raistrick, A., and Marshall, C. E., *The Nature and Origin of Coal and Coal Seams*, The English Universities Press, London, 1939, pp. 178-205, 271.

TABLE V
TYPE CLASSIFICATION OF COAL ³⁶

	High Proportion of Translucent Material.	High Proportion of Opaque Material.
Macroclastic	<p><i>Clarain (Bright or Soft Coal)</i> Well-laminated coal with a high proportion of vitrinite bands and fragments together with some resins, spore exines, cuticles and a little fusinite.</p>	<p><i>Durain (Dull or Hard Coal)</i> Lamination ill defined except where marked by thin shredlike vitrinite bands. High proportion of fusinite in lenticles, irregular fragments and minute grains, together with resins, microspores, megaspores, and cuticles. In some varieties the spore content may be very high. (Spore coals.)</p>
Microclastic (very fine grained)	<p>Decrease in average size of plant remains</p> <p><i>Cannel (Parrot).</i> Greasy luster. Lamination practically absent. Plant debris highly comminuted with many minute vitrinite and other fragments.</p> <p>↕</p> <p><i>Algal Cannels.</i> Similar to cannels. Greasy luster. Lamination poor or absent. Constitution as cannels but algae are not uncommon.</p> <p>↕</p> <p><i>Bogheads and Torbanites.</i> Similar to cannels, but as the content of algae rises, the luster is lost and the coal tends to become brown.</p>	

³⁶ See p. 201 of ref. 35.

TABLE VI

NOMENCLATURE OF COAL PETROLOGY ³⁷

British and German terminology as recommended by the International Committee at Heerlen, 1935. Corresponding American terms are those used by the U. S. Bureau of Mines

Macroscopic Character of the Coal	British Nomenclature		German Nomenclature		American Nomenclature	
	Rock Types	Macerals (Constituents)	Steifenarten	Gefügebildungsstufe	Coal Types	Constituents
Uniform brilliant black bands	VITRAIN	<i>Vitrinite</i> : translucent in thin section; cellular structure may or may not be well preserved: (a) <i>Collinite</i> —structureless (b) <i>Tellinite</i> —structure preserved: (i) <i>Xylinite</i> —formed from wood tissues (ii) <i>Perkinite</i> —formed from cortical tissues (iii) <i>Suberinite</i> —formed from cork tissues	<i>Vitrit</i>	<i>Vitrinit</i>		<i>Anthraxylon</i> . Term used to include the uniform brilliant bands (or their counterparts) in coals of all ages
Charcoal-like layers and fragments which readily soil the fingers	FUSAIN	<i>Fusinite</i> : cell structure well preserved. Cell walls opaque; cell cavities either empty or occupied by mineral matter	<i>Fusit</i>	<i>Fusinit</i>		<i>Fusain</i>
Bright Coal: clearly laminated; composed of innumerable brilliant fragments and bands with some duller material	CLARAIN	Containing: <i>Vitrinite</i> <i>Resinite</i> —resin bodies <i>Exinite</i> —which includes— (i) <i>Cutinite</i> —from cuticles (ii) <i>Sporinite</i> —from spores together with a little <i>Micrinite</i> —granular opaque matter <i>Fusinite</i> —as above	<i>Clarit</i>		BRIGHT COAL	Containing: <i>Anthraxylon</i> } Translucent <i>Spores</i> } Attritus <i>Cuticles</i> } <i>Resins</i> , etc. } together with <i>Opaque and semi-translucent attritus</i> <i>Fusain</i>
Dull Coal: dull and nonreflecting in the hand specimen; lamination poor or absent	DURAIN	Containing: <i>Fusinite</i> <i>Micrinite</i> <i>Resinite</i> <i>Exinite</i> (i) <i>Cutinite</i> (ii) <i>Sporinite</i> and a very little <i>Vitrinite</i>	<i>Durit</i>		SEMI-SPLENT COALS SPLENT COAL	Intermediate in properties and constitution between bright and splint coal Very largely <i>opaque and semi-translucent attritus</i> with <i>spores, cuticles, resins</i> , and a little <i>anthraxylon</i>

³⁷ See p. 271 of ref. 35. Vitrinite and fusinite according to the International Congress can be regarded as rock types (a view which was not adopted in the text of this book), although the distinction between vitrain and vitrinite, and fusain and fusinite, is not defined.

and macroclastic and microclastic varieties were differentiated. Clarain (bright or soft coal) stood alone in the macroclastic group. All bright coal was designated as clarain and contains vitrain bands of greater or less thickness, this coal being composed of vitrinite. "Clarain, the coal type," it was stated, "is thus the counterpart of the rock type of the geologist, and vitrinite corresponds to one of the rock-forming minerals. . . . Vitrinite is thus a 'maceral' and a most important one." The authors accordingly substituted the term vitrinite for vitrain, and spoke of vitrinite bands rather than of vitrain, although they apparently realized that the term vitrain will have to be recognized as an alternative term, but with the meaning of the term vitrinite. According to this system of terminology, vitrinite bands are identified as equivalent to the anthraxylon of Thiessen. The authors stated:

as a result of the refinement of technique in preparing thin sections it has been possible to demonstrate that not only do the vitrinite bands of the British bituminous coals retain their original cell structure in varying degrees of perfection, but also that these structures are practically identical with those of the anthraxylon bands in American coals of Carboniferous age.³⁸

Clarain (bright coal), besides containing vitrinite, not uncommonly in bands of considerable thickness, contains also "a large proportion of smaller components." Megaspores, microspores, cuticles, and isolated resins were mentioned as among the components easily recognized. Fusain, which was called fusinite, was also included among the components of clarain, as was also "micronite," the name Stopes applied to what Thiessen appears to have designated the "opaque attritus."³⁹ Clarain, it ap-

pears, is characterized by a banded appearance; the name was used as essentially synonymous with "bright banded coal" and, therefore, includes both clarain and vitrain of Stopes and of the Heerlen Congress, and the anthraxylon and translucent attritus of Thiessen.

Coals of the microclastic group, according to Raistrick and Marshall, are characterized by their fine-grained texture; the group includes durain, cannel coal, algal or boghead coals, as well as common cannel (parrot) coals. Durain is characterized by the presence of much opaque material, "owing to the high proportion of fusinite, micronite, and other semi-opaque constituents."⁴⁰

METHODS OF RESEARCH IN COAL PETROGRAPHY

PREPARATION TECHNIQUE

The technique of microscopic research bearing on the petrography of coal has become essentially stabilized during the past twenty years. At present the prevailing methods of examining coal microscopically are: the thin-section method; the metallographic method using polished surfaces; the same method using etched surfaces or surfaces that are relief polished; and finally the maceration method for examining the more resistant components of the coal after the selective removal of the more soluble constituents, particularly the humic matter.

Thin Sections. The technique of microscopic study of thin sections of coal involves first the methods of preparation of material for study. The preparation of thin sections has been described by Thiessen, Sprunk, and O'Donnell.⁴¹ No thin-

⁴⁰ See p. 195 of ref. 35.

⁴¹ Thiessen, R., Sprunk, G. C., and O'Donnell, H. J., *U. S. Bur. Mines, Inf. Circ. 7021* (1938), 8 pp.; *Fuel*, **17**, 307-15 (1938).

³⁸ See p. 181 of ref. 35.

³⁹ See pp. 193-4 of ref. 35.

section technique superior to that used at the Bureau of Mines has been developed.

Polished Surfaces. The technique of polishing surfaces of coal to study by metallographic methods originated with Winter⁴² and was later modified to the extent of etching the polished surface with Schultze's reagent to bring out the structure. The polishing method was employed by Légraye.⁴³ Seyler⁴⁴ also used polished surfaces, employing a method essentially that devised and used by Sorby for metallography. Duparque is the outstanding advocate of the "simple polished surface," which is fully described in his work on the microscopic structure of the coals of Nord and Pas-de-Calais.⁴⁵

In discussing the objections that have been raised against the method of simple polishing, Duparque pointed out that the three main reasons for unsatisfactory specimens are the formation of an undesirable specular polish which conceals the underlying coal structure, the fouling of the surface by foreign material, and the presence of scratches. Duparque did not approve of relief polishing advocated by Stach.

The high quality of Duparque's skill in the preparation of polished surfaces and in their photography is indicated by Figs. 6 to 13 shown on pages 109 to 116. These photographs represent unetched, simple polished surfaces and were obtained by the use of the metallographic type of microscope and reflected light.

Relief Polishing and Etching. Winter, Stach, Jongmans, Roos, and others have

modified polished-surface technique by relief polishing or by relief etching. Stach⁴⁶ is the outstanding exponent of relief polishing. His *Kohlenpetrographisches Praktikum* is essentially an exposition of this method. Stach also has used the relief-polishing technique in the study of fine coal and dust.⁴⁷

The etched-surface technique employed by Koopmans, Jongmans, and Roos has been described by Roos.⁴⁸ After polishing and relief etching, following in general the method employed by Stach except that no laps are used, the specimen is allowed to dry out for several days, after which it is acid etched. The specimen is cut in two pieces, one of which is acid etched in a mixture of 10 cc. concentrated sulfuric acid and 30 cc. saturated solution of chromic acid. (See Fig. 3.) Iwasaki and Hsieh have also described the acid etching method.⁴⁹

Maceration. The maceration method was introduced by Schulze⁵⁰ and improved by von Gümbel.⁵¹ The method was also used and improved by Thiessen.⁵² (See also Bode.⁵³)

⁴⁶ Stach, E., *Kohlenpetrographisches Praktikum*, Gebrüder Borntraeger, Berlin, 1928, p. 65; *Mitt. Abt. Gesteins-, Erz-, Kohle-, und Salzuntersuch. preuss. geol. Landesanstalt*, **2**, 75-94 (1927).

⁴⁷ Stach, E., *Lehrbuch der Kohlenpetrographie*, Gebrüder Borntraeger, Berlin, 1935, pp. 227-55.

⁴⁸ Roos, G., *Compt. rend. deuxième congr. l'avance. études strat. Carbonifère, Heerlen, 1935*, **2**, 1100 (1937).

⁴⁹ Iwasaki, C., *Fuel*, **8**, 143-4 (1929). Hsieh, C. Y., *Arb. Inst. Paläobotanik Petrog. Brennst. preuss. geol. Landesanstalt*, **2**, 25-37 (1930).

⁵⁰ Schulze, F., *Ber. k. Akad. Wiss. Berlin*, **1855**, 676-8.

⁵¹ Von Gümbel, C. W., *Sitzber. math.-physik. Klasse Akad. Wiss. München*, **13**, 111-216 (1883).

⁵² Thiessen, R., *U. S. Bur. Mines, Bull.* **38**, 216-8 (1913).

⁵³ Bode, H., *Berg. Tech.*, **21**, 305 (1928); *Fuel*, **8**, 86-90 (1929).

⁴² Winter, H., *Glückauf*, **49**, 1406-13 (1913); *Fuel*, **2**, 78-82 (1923).

⁴³ Légraye, M., *Ann. soc. géol. Belg.*, **51B**, 145-7 (1928).

⁴⁴ Seyler, C. A., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Phys. Chem. Surv. National Coal Resources*, **16**, 6 (1929).

⁴⁵ Duparque, A., *Mem. soc. géol. Nord*, **11**, Pt. I, 35-51 (1933).



FIG. 3. A comparison of etched (left side) and unetched (right side) coal surfaces. The coals shown increase in rank from No. 7 to No. 12. ($\times 30$.) After Roos.⁴³

Schopf⁵⁴ has described the maceration method in a discussion of the spores of Herrin (No. 6) coal in Illinois. The general procedure involved the oxidation of the ulmic material in the coal and its removal by alkalis. Lignites and brown coals do not require oxidation in order to dissolve the ulmins and thereby release the waxes and resins and other less soluble residues. On the other hand, high-rank bituminous coals and anthracites show little if any response to oxidizing agencies. The maceration procedure is, therefore, not satisfactory for such coals. Schopf referred to a summary of the present-day maceration methods by Jurasky⁵⁵ and to descriptions of methods published by Zetzsche and Kälin,⁵⁶ by Zerndt,⁵⁷ and by Sahabi.⁵⁸

Study of Coal Dusts. One other technique that has been given some attention is connected with the study of coal dusts and fine coals. The purpose of such studies is the identification of the components of the dust in terms of the banded ingredients or macerals (phyterals). The problem of preparation is to find the most convenient way of handling the material. There are two prevailing procedures. Some technicians prefer to examine the fine material as loose fragments and to make determinations, separations, and counts by manual manipulation, after the method employed in making counts of any fine material of varying composition.⁵⁹

Identification of particles in terms of ingredients depends upon ocular inspection and the experience and skill of the operator, and also upon the purity of the individual fragments. One of the uses of this method is the estimation of the fusain content of de-duster dust and washery refuse.⁶⁰

Another method used and advocated mainly by European technicians involves the formation of some sort of briquet so that the coal is in a more or less solid form which can be cut and polished. Stach,⁴⁷ one of the chief advocates of this method of studying fine coal and coal dusts, has suggested three methods of preparing the coal for examination, which he calls the molding, the impregnation, and the compression methods. In the first two the coal is mixed with a wax called Schneiderhöhn's mixture. In the molding method the powdered wax and coal are mixed cold and then heated in a small mold until the wax melts, after which the mixture is cooled to form a small block. In the impregnation method the coal powder and wax are heated separately, the coal being added to the melted wax or the melted wax poured on the coal. Apparently more coal can be used in proportion to the wax in this method than in the molding method, resulting in a closer spacing of the coal particles (Fig. 4). In the compression method, the coal is made into a more or less solid briquet either by compaction or impact.

Piersol⁶¹ has formed impaction and compaction briquets which, although no binding material is used, are sufficiently solid to saw and polish much as the original coal. The physical constitution of such

⁵⁴ Schopf, J. M., *Illinois State Geol. Survey, Rept. Investigations*, 50, (1938), p. 8.

⁵⁵ Jurasky, K. A., *Handb. biol. Arbeitsmethoden*, 11, Teil 4, Heft 2, 331-52 (1931).

⁵⁶ Zetzsche, F., and Kälin, O., *Braunkohle*, 31, 345-51, 363-6 (1932).

⁵⁷ Zerndt, J., *Acad. polon. sci., Comité pub. silésiennes, Trav. Géol.*, No. 1, p. 3 (1934).

⁵⁸ Sahabi, Y., dissertation, Lille, 1936, 64 pp., especially 14 and 18.

⁵⁹ Taggart, A. F., *Handbook of Ore Dressing*, John Wiley & Sons, New York, 1927, p. 1193.

⁶⁰ Parks, B. C., and McCabe, L. C., *Illinois State Acad. Sci.*, 33, No. 2, 164-81 (1940).

⁶¹ Piersol, R. J., *Illinois State Geol. Survey, Rept. Investigations* No. 31, 1933, 70 pp.

briquets has not been studied to any extent.

The preparation of embedded coal specimens for laboratory study has been much simplified because of the recent availability of thermoplastic powders from which either

MEGASCOPIC TECHNIQUE

Megascopic technique consists mainly in the identification and quantitative measurement of the banded ingredients observed with the unaided eye. For such studies,



FIG. 4. On the left is a polished and etched surface containing fragments of *Gasflammkohle* prepared by molding (*Gusschliff*); on the right is a similar surface of fragments of Peisenberg pitchcoal made by the impregnation methods. (*Trankschliff*). Oil immersion. ($\times 200$.) After E. Stach.⁴⁷

opaque or transparent mounts can be quickly prepared using a specially heated hydraulic press. The coal dust and thermoplastic powder are mixed in the dry state in the proportion desired, and the mixture is placed in an electrically heated mold assembly on the hydraulic press and compressed and heated for a few minutes, thereby providing a mount in which the coal fragments possess circumambient visibility if a transparent thermoplastic (Lucite) is used.

columns cut from the coal seam are generally used, one surface usually being smoothed and polished to make identification possible. From such columns, profiles are prepared which provide a basis for delineation of the physical composition of the coal, either graphically or photographically, and for physical analysis in terms of the banded ingredients. Such profiles can, of course, also be prepared on the basis of microscopic examination, and, usually, the published profile represents

the results of both microscopic and megascopic determinations.

Drath and Jaskólski⁶² have published a diagrammatic megascopic profile of the Otto coal seam, Upper Silesia. Roos⁶³ has published numerous profiles of a coal seam in the South Limburg region in the Netherlands. Coal-seam profiles accompany the descriptions of coal seams prepared by R. Thiessen and his associates in connection with the studies of coke-, gas-, and byproduct-making properties of a number of American coals.⁶⁴ Kühlwein⁶⁴ and associates have presented profiles of the Ruhr coals. Koopmans⁶⁵ has published profiles of certain Netherlands coal seams; and many profiles of English coal seams have been published in the reports of the Physical and Chemical Survey of the National Coal Resources.⁶⁶ McCabe⁶⁷ and associates have used the profile method to determine the percentage of banded ingredients in (Herrin) No. 6 Seam coal in southern Illinois.

USE OF X-RAYS

X-ray shadow pictures have had considerable use as a graphical means of differentiating between the various banded ingredients. Kemp⁶⁸ has probably provided the best description of the technique together with a bibliography of earlier articles. Kemp used blocks of coal cut into

slabs of uniform thickness of half-inch and took ordinary and stereoscopic radiograms (Fig. 5).

The use of radiograms to indicate the amount of impurities present in coal has been suggested by several investigators.⁶⁹

Beeching⁷⁰ (1938) made radiographs of slabs of coal that had been soaked in a solution of lead salts. The general result was to show more clearly the planes and loci representing open cavities in the coal. For coal petrography, the significance of the method is not apparent.

The behavior of coal and of the coal ingredients with respect to X-rays, the interpretation of X-ray diffraction patterns, and other X-ray phenomena are discussed in the section dealing with the physical properties of coal. (See Chapter 7.)

REACTION TO PHOTOGRAPHIC PLATES

Stopes⁷¹ has briefly called attention to the differences in the reaction of the banded ingredients when placed in contact with photographic plates. Vitrain was found to make the most intense image. The procedure appears to have no particular value as a means of identifying the ingredients.

MICROSCOPIC TECHNIQUES

Polished and Polished-and-Etched Surfaces. The satisfactory study of simple polished surfaces of coal that have not been etched requires a microscope of the

⁶² Drath, A., and Jaskólski, S., *XII Ann. Polsh Geol. Soc., Krakow*, 1936, 685-761.

⁶³ See pp. 1057-161 of ref. 17.

⁶⁴ Kühlwein, F. L., *Compt. rend. deuxième congr. l'avance. études strat. Carbonifère, Heerlen*, 1935, 2, 539-601 (1937).

⁶⁵ Koopmans, R. G., *ibid.*, 2, 523-6.

⁶⁶ Dept. Sci. Ind. Research, *Fuel Research, Phys. Chem. Surv. Nat. Coal Resources*, Nos. 3-6, 10, 13, 18, 19, 21, 22, 24, 25, 27, 30, 34, 35, 36, 38-43, 45-47, 1923-39.

⁶⁷ McCabe, L. C., Mitchell, D. R., and Cady, G. H., *Illinois State Geol. Survey, Rept. Investigations* 34, 1-44 (1934).

⁶⁸ Kemp, C. N., *Proc. Roy. Soc. Edinburgh*, 48, 167-79 (1929).

⁶⁹ Chance, H. M., *Fuel*, 3, 213-7 (1924). Castelli, G., *Rass. min. met. chim.*, 63, 25-32 (1925). Lessing, R., *Fuel*, 5, 17-23, 69-76, 117-24, especially p. 23 (1926). Sinnatt, F. S., *Fuel Econ. Rev.*, 6, 9-11 (1927). Louis, H., *The Preparation of Coal for the Market*, Methuen & Co., London, 1928, 217 pp. Stach, E., *Mitt. Abt. Gesteins-, Erz-, Kohle-, und Salz-Untersuch. preuss. geol. Landesanstalt*, No. 4, 1-23 (1928). Van Aubele, R., *Rev. ind. minérale*, No. 177, 163-70, 189-95, 1928. Mitchell, D. R., *Univ. Illinois Eng. Exp. Sta., Bull.* 258, 21-25 (1933).

⁷⁰ Beeching, R., *J. Inst. Fuel*, 11, 240-2 (1938).

⁷¹ See p. 475 of ref. 16.



FIG. 5. Radiograph of a slab of bituminous coal. After Kemp.⁶⁸

metallographic type. The use of this instrument necessitates the production of an absolutely plane, highly polished surface which is placed at right angles to the axis of the microscope. The method is most satisfactorily applied to the higher-rank coals such as high-rank bituminous coals and anthracite, which, on the other hand, are less amenable to other methods of

preparation. The outstanding exponent of the metallographic method for simple polished surfaces is Duparque.²⁷

The petrographic components revealed by this method are, in the main, the same as those revealed by other techniques, and in general they are similarly interpreted in terms of plant tissues. Components particularly clearly revealed because of the

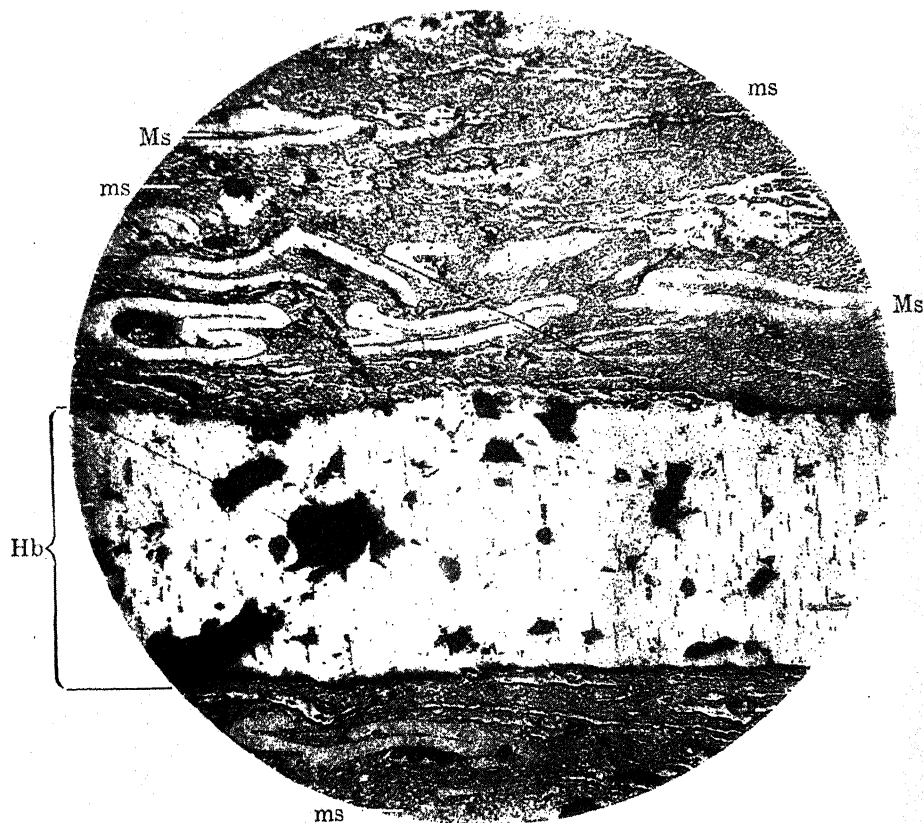


FIG. 6. A portion of a polished surface of bituminous coal (*houilles sèches à longue flamme*) showing a band of vitrain (*Hb*) (*houille brillante*) between two layers of durain (*houille mate*). The upper half of the picture shows durain containing numerous megaspores (*Ms*). Duparque stated that all the space between the megaspores is occupied by a felting (*feutrage*) of microspores (*ms*) embedded in an amorphous groundmass (*ciment*). ($\times 50$.) After Duparque.²²

slight differential effect of polishing are the materials having an original waxy or resinous composition such as spore exines (Fig. 6), cuticles (Fig. 7), resinous bodies (Figs. 8 and 9), resins in vitrain bands (Fig. 10), fusain (Fig. 11), bogen structure (Fig. 12), and cell structure in vitrain (Fig. 13).

Certain American coals have been described and studied by Fanshaw,⁷² employ-

ing the Duparque technique of simple polishing and the metallographic microscope for observation and photography.

Polished surfaces that have been modified by relief polishing, or by etching by any of the possible methods, may be examined by the metallographic microscope, this being the type of microscope pre-

⁷² Fanshaw, J. R., dissertation, Lille, 1930.

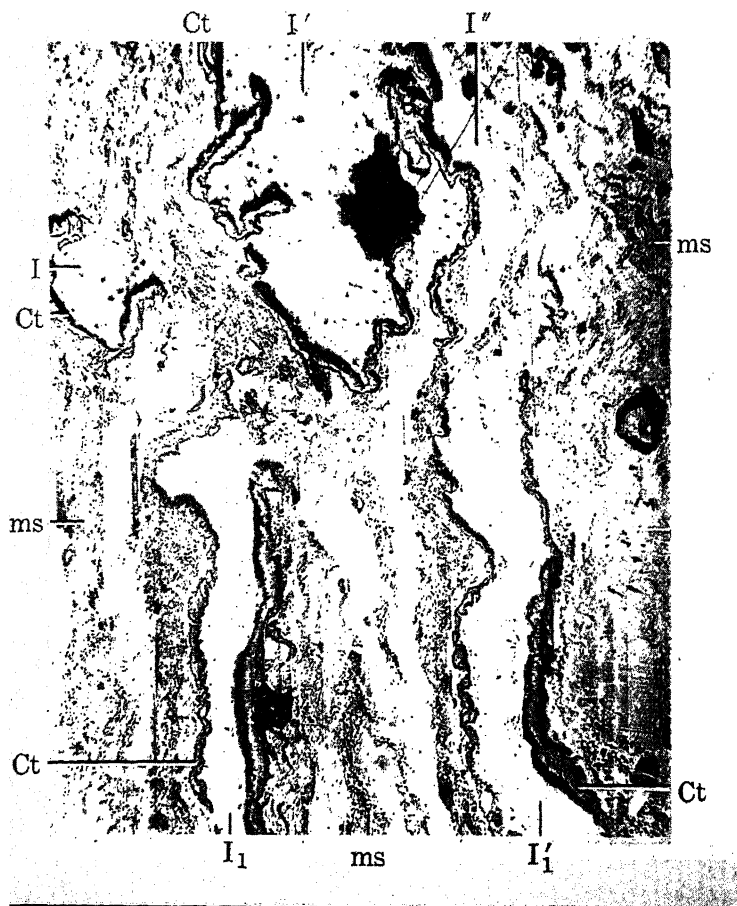


FIG. 7. Polished surface of a high-volatile (volatile matter, 34.5 percent) bituminous coal (*houille grasse à gaz*), showing a number of cuticles (*Ct*). The clear areas between the cuticles (*I*) were believed by Duparque to be jellified leaf tissue. The ground mass is "rich in microspores" (*ms*). ($\times 55$) After Duparque.²⁷

ferred by Winter,⁴² Stach and Kühlwein,⁷³ Stach,⁴⁶ Roos,¹⁷ and others.

The results obtained by Roos in the photography of etched polished surfaces are shown in Figs. 3 (see page 104), 14, and

graphs 13, 14, 15, and 16). Bright coal will sometimes show organic structures (Fig. 15, photographs 17 and 18), but not uncommonly it appears brilliant and without structure and is called collain (Fig. 16).

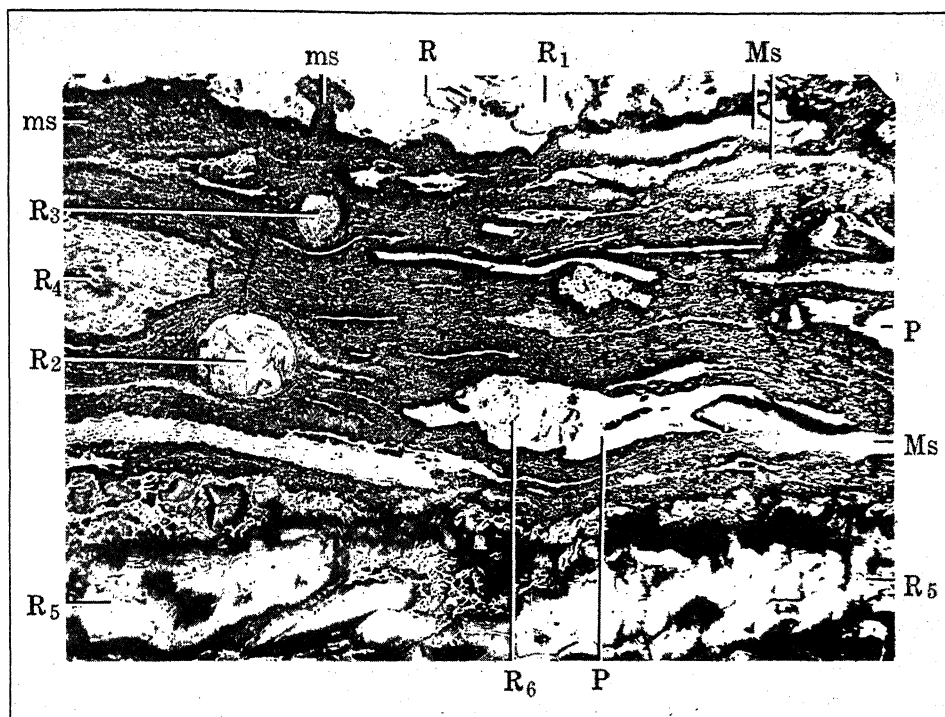


FIG. 8. Polished surface of a high-volatile bituminous (volatile matter, 42.75 percent (*houille sèche à longue flamme flénu sac*), described by Duparque as a durain "very rich in microspores (*ms*) and containing numerous resinous bodies (*R*)."²⁷ *R*₁, *R*₂, and *R*₃ were described as round, unflattened resinous bodies; *R*, *R*₄, and *R*₅ were identified as fossilized (resinized) tissues; and *R*₆ as a resinous body analogous to *R*₁, *R*₂, and *R*₃ but more or less disintegrated and mixed with cement (*P*). (×55.) After Duparque.²⁷

15.¹⁷ Figure 14 shows particularly well the shapes of spore exines (photographs 27, 28, and 29) and of cuticles (photographs 31, 32, 33 and 34). Photograph 30 was described as a piece of telainized wood tissue (anthraxylon?). In Fig. 15, fusain is clearly differentiated by etching (photo-

Within the last ten years the ultropak type of equipment has found some application for the examination of polished-and-etched surfaces. Its particular advantage is that colors of the various components, as well as shapes, aid in their identification, particularly if the coal is viewed under immersion. Even so the colors are far less effectively shown than they are in thin sec-

⁷³ Stach, E., and Kühlwein, F. L., 25, 842-5 (1928).

tions. This advantage does not usually extend to photography unless film to reproduce colors is used.

Kühlwein, Hoffmann, and Krüpe⁷⁴ have discussed at considerable length the elaborate universal microscopic equipment (Panphot, E. Leitz) for the study of polished-and-etched surfaces, which permits

respect to the differentiation and identification of the coal components.⁷⁵

The polarizing microscope has been recommended by several investigators⁷⁶ for studying polished or polished-and-etched surfaces of coal.

The use of polarized light and the polarizing microscope, as explained by Hsieh,⁷⁶

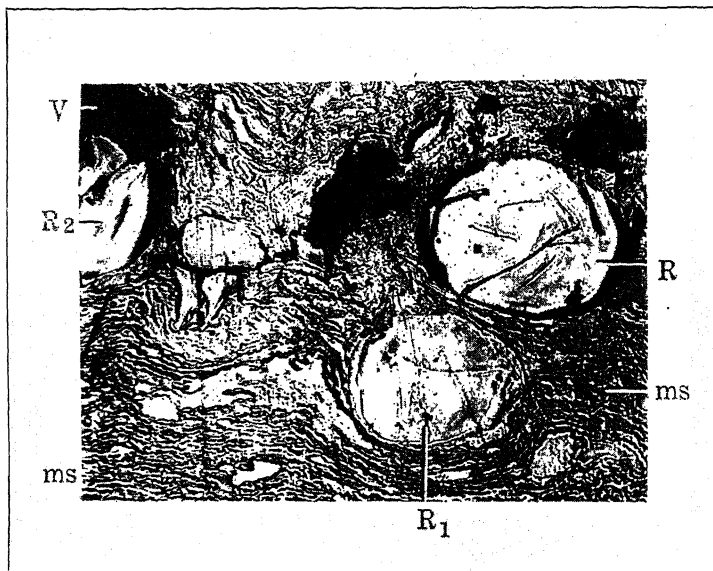


FIG. 9. Polished surface of a high-volatile coal (volatile matter, 35.5 percent) (*houille grasse à gaz*). The illustration shows a group of resinous bodies (*R*) in a groundmass composed mainly of microspores (*ms*). ($\times 250$.) After Duparque.²⁷

the use of integrating stages, monocular and binocular tubes, polarized light, arrangements for photography, etc. These writers also have called attention to the dual or "comparing microscope" for the close comparison of similar forms, of mixtures of coal, and of rank differences of the same type of coal. Doubt exists whether such elaborate equipment is necessary to attain all the results desired with

depends upon the anisotropism of coals. Anisotropism increases with the rank of the coal, so that any advantage that exists for polarized light over unpolarized light increases with rank. Hsieh claimed that polarized light in the study of polished sur-

⁷⁵ See p. 1086 of ref. 17.

⁷⁴ Kühlwein, F. L., Hoffmann, E., and Krüpe, E., *Glückauf*, **70**, 777-84 (1934).

⁷⁶ Hsieh, C. Y., *Geol. Soc. China, Bull.* **9**, 311-20 (1930). Hoffmann, E., *Glückauf*, **68**, 523 (1932). Hoffmann, E., and Jenkner, A., *ibid.*, **68**, 81-8 (1932). Seyler, C. A., *Colliery Guardian*, **155**, 990-4, 1046-8, 1087-9, 1137-9 (1937); *Proc. S. Wales Inst. Engrs.*, **53**, 254-327 (1938); *Fuel*, **17**, 177-86, 200-9, 235-42 (1938).

faces of anthracite served to reveal the vegetable tissues as effectively as the flame etching of Turner.⁷⁷

Hsieh, Hoffmann, McCabe, and Quirke,⁷⁸ and others have taken the polarizing effect

light.⁷⁹ The purposes of the lens, according to Hsieh,⁷⁶ are (1) to increase the detail and fineness of the image when examined with strong illumination; (2) to detect, in an approximate way, the rate of

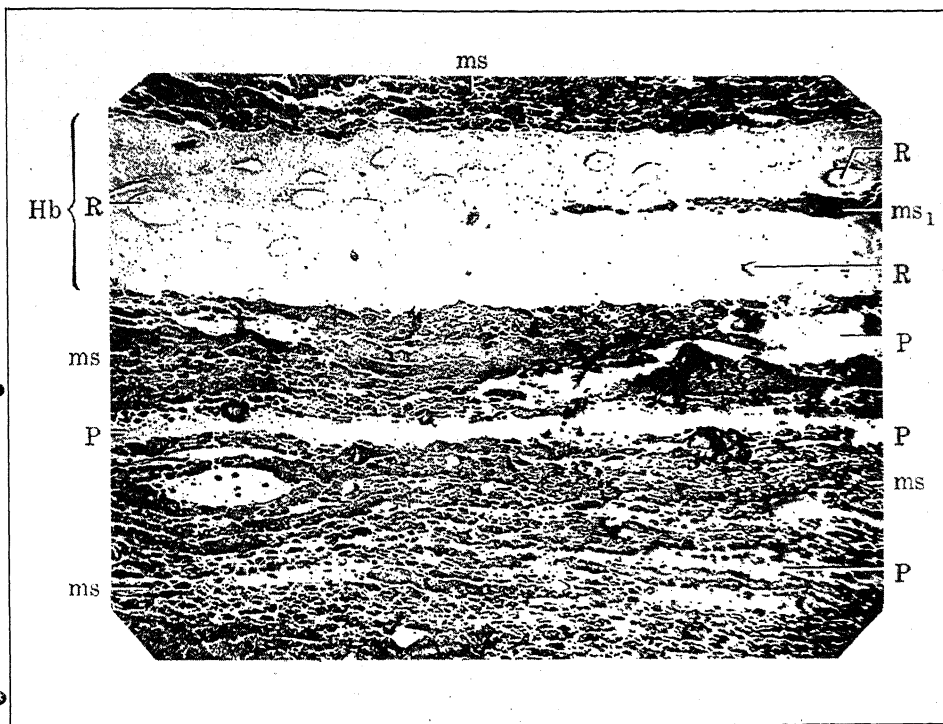


FIG. 10. Polished surface of high-volatile bituminous coal (volatile matter, 38.18 percent) (*houille grasse à gaz*), showing an intercalation of a band of vitrain (*Hb*) containing resin bodies (*R*) between two bands of durain (*houille mate*). There are microspores (*ms*) in the durain and a large amount of pâte (*P*) (cement or fundamental matter). ($\times 50$.) After Duparque.⁷⁷

of polished surfaces of coal as an index of coal rank, as is explained in Chapter 7.

Considerable importance is placed upon the oil-immersion lens in the study of polished surfaces with or without polarized

decrease of reflecting power; and (3) to detect internal reflection colors.

Microscopic study of polished and of polished-and-etched surfaces provides a basis for the identification of the petrographic components and for the classification of coal on the basis of its physical constitution in the terms of such components.

⁷⁷ Turner, H. G., and Randall, H. R., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 127-48 (1925); *J. Geol.*, **31**, 306-13 (1923).

⁷⁸ Quirke, T. T., and McCabe, L. C., *Bull. Geol. Soc. Am.*, **49**, 669-82 (1938).

⁷⁹ Stach, E., *Glückauf*, **73**, 330-3 (1937).

The varieties of vitrain, structureless and that showing structure, are usually recognized by those employing this technique in accordance with the classification proposed at the Second Heerlen Congress, 1935.

THIN SECTIONS

The microscopic technique followed in the study of thin sections is relatively simple. A good high-power microscope and good illumination are the essential require-

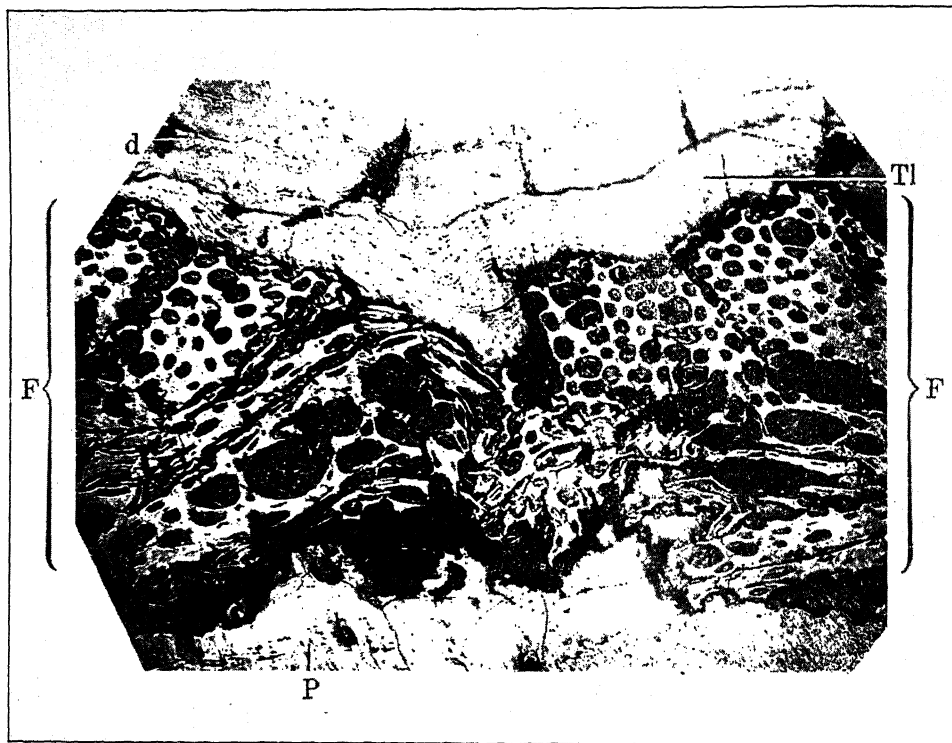


FIG. 11. Polished surface of a high-volatile bituminous coal (volatile matter, 34.5 percent) (*houille grasse à gaz*), showing a band of vitrain (xylain passing into xylovitrain) at the top (*TL*), resting upon an irregular band of fusain (*F*). Duparque believed that the fusain shows evidence of having been plastic before it was solidified. At the bottom is a body of amorphous cement (*P*). ($\times 250$.) After Duparque.²⁷

(See page 98.) A relatively recent description of coal based upon this technique is that of Drath and Jaskólski⁶² of the Otto coal seam, Upper Silesia. The sort of physical analysis given is typical of the contributions to petrography and description of European technicians who work with polished and etched surfaces.

Some laboratories have elaborate instruments in which the source of illumination is fixed in the stand. Others have found simpler apparatus satisfactory.

The comparative simplicity of thin-section microscopy of coal arises from the relative ease of differentiation of the various components of coal and the usual dis-

tininess of the organic structures in a well-prepared thin section. The preparation of the thin sections is probably the main "bottle-neck" in the technique. Photography of polished and polished-and-etched surfaces reproduces fairly accurately what the eye observes since distinctions are mainly those involving lighting rather than color, but photographs of thin sections, unless they are made and reproduced in color, do not do this. Differences in color which are important in the differentiation of components are not shown. Reproductions of photographs of thin sections are, therefore, not always distinguishable from reproductions of photographs of polished surfaces, whereas, if the colors were reproduced, there would be no question about the source of the photograph.

Except for coals of low-volatile and higher rank, from which it is very difficult to make thin sections, the thin-section technique is regarded in America and generally in England as preferable to the polished-surface or the polished-and-etched-surface technique.

OBJECTIVES OF PETROGRAPHIC STUDIES

The primary purpose of the microscopic study of coal is the identification of the components of coal. The purposes of such identification differ. If the purpose of the study is mainly petrographic, then presumably the identification will be petrographic, and the components will be thought of as coal material. On the other hand, if the point of view is chiefly paleobotanical, the components are mainly of paleobotanical interest. Coal petrography has not become sufficiently well organized in technique and terminology for the fields of paleobotany and of petrography to have become definitely separated. Some writers emphasize the petrographic and others the paleobotanical aspect of coal

microscopy. In addition to this confusion is the difficulty of nomenclature as employed by those using thin sections and those using polished and polished-and-etched surfaces for examination.



FIG. 12. Crushed fusain or "bogen structure" as it appears in a polished surface under high magnification. ($\times 780$.) After Duparque.²⁷

A systematic science of coal petrography will eventually rely upon a standard microscope technique for description, definition, and nomenclature for the varieties of coal. Such standardization has not yet been achieved.

PALEOBOTANICAL STUDIES

Coal petrography is closely related to coal paleobotany because of the definite identification of the physical components

of coal as representing initial plant tissues, organs, or secretions. Whether one is studying coal from the standpoint of the coal petrographer or from that of the paleobotanist, it is desirable to understand the

with respect to their botanical significance. A large amount of literature, therefore, deals with the botanical significance of the macerals (or phyterals) present in coal.

Space will not permit more than a brief

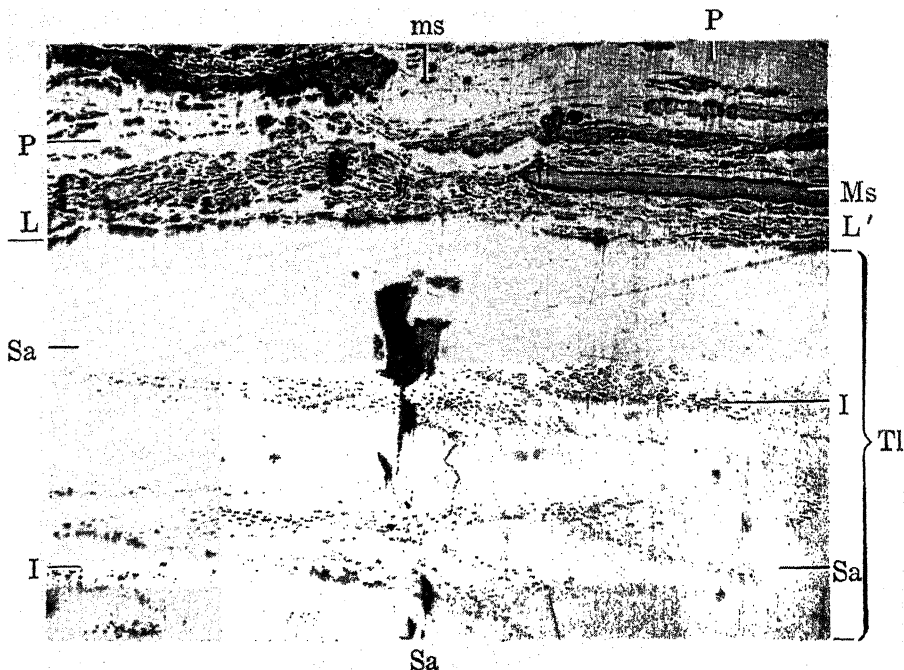


FIG. 13. Polished surface of a high-volatile bituminous coal (volatile matter, 33.60 percent) (*houille grasse à gaz*), composed mainly of vitrain (*TI*) in which islets of cell structure (*I*) can be seen. Most of the vitrain appears "amorphous" (*Sa*). In the upper part of the picture there are one large spore (*Ms*) and a considerable amount of cement (*P*). A microspore is indicated by the symbol (*ms*). The upper band Duparque called clarain. ($\times 55$.) After Duparque.²⁷

botanical significance of the components of the "coal conglomerate," as it has frequently been called. The fact that the study of coal has commonly been carried on by students who are botanically trained has resulted in overemphasis of the botanical side of coal petrography, and studies have been directed largely toward the interpretation of the constituents of the coal

consideration of the nature of paleobotanical studies that have been directed toward the discovery, isolation, identification, description, and classification of the various fossil plant forms (phyterals) that have been found in coal.

Plant entities present and identifiable in coal may be conveniently grouped under six headings: spore exines, cuticles, algae,

fungi, unorganized resins and waxes, and wood or bark tissues. The wood and bark tissues and some of the resinous material are found in the vitrain (anthraxylon) bands or lenses; the other tissues or organs compose a large part of the clarain and

be recognized in thin sections and in polished-and-etched surfaces.

The character of the spores obtained from bituminous coal by maceration is illustrated by the forms shown in Fig. 17, all of which were isolated from Herrin

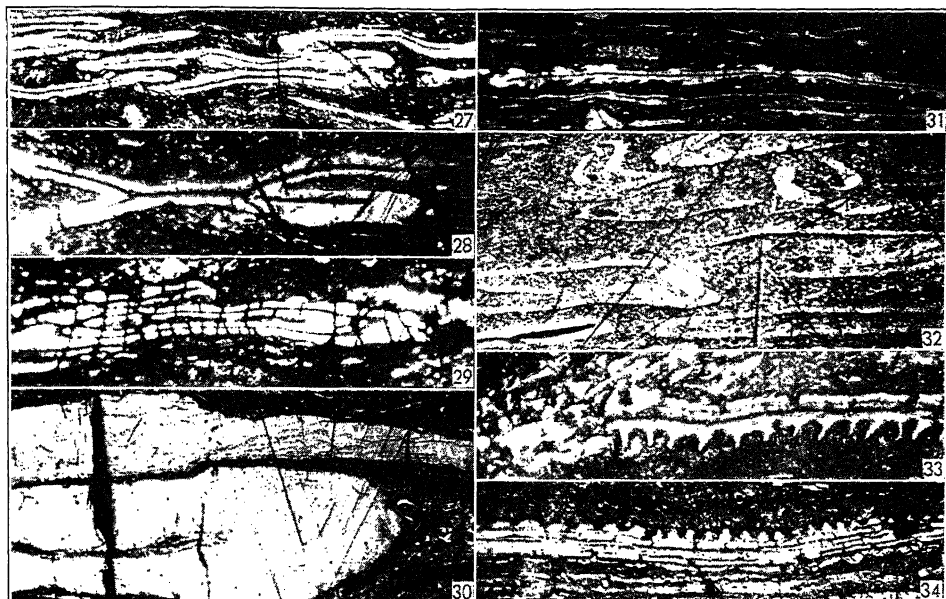


FIG. 14. A series of photographs showing "some different forms in which plant tissues may be found in coal." Photographs 31, 32, 33, and 34 were said to represent cuticles. Photographs 27, 28, and 29 show megaspore exines, and 30 was thought by Roos to be a fragment of "telainized wood tissue." (Photographs 27, 29 to 32 inclusive, and 34, $\times 50$; 28 and 33, $\times 100$.) After Roos.¹⁶

durain that are the attrital part of coal. Numerous attempts have also been made, with varying success, to discover the botanical significance of opaque matter characteristic of durain or splint coal.

The study of spore exines as paleobotanical entities and as a basis for taxonomic and stratigraphic studies has long been under way, particularly in Europe. The purpose of these studies has been mainly to identify and classify the forms that could be isolated from the coal or could

(No. 6) coal seam in southern Illinois, except photograph 55, which came from Colchester (No. 2) coal seam in northwestern Illinois.⁵⁴

Like spores, the fragments of cuticles of leaves and stems are recovered in more or less unmodified form when coal is subjected to maceration. They have received considerably less attention from paleobotanists than have spores. Among the coals in which cuticular remains are particularly important is the so-called Moscow paper

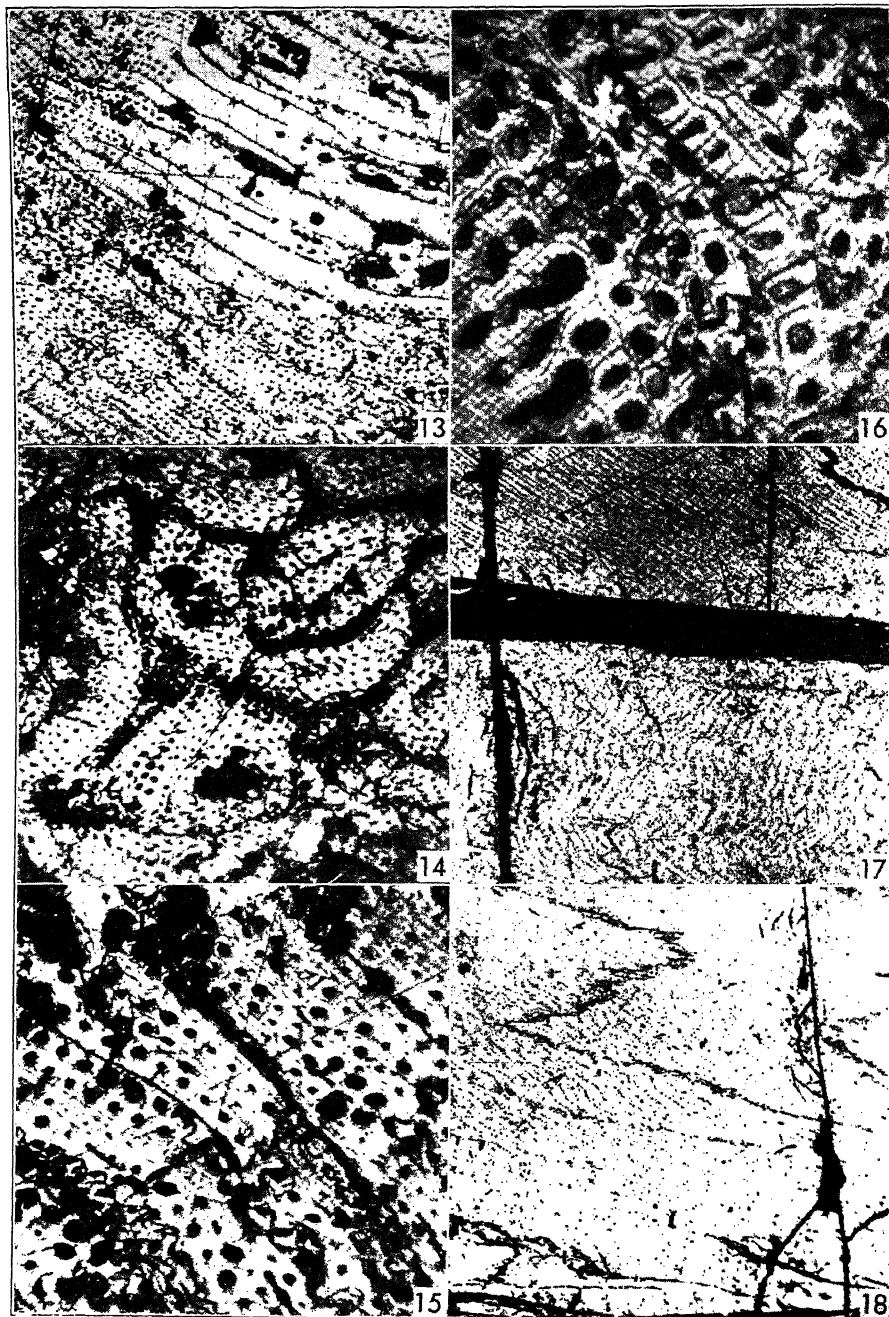


FIG. 15. Polished and etched surfaces of fusain or semi-fusain (photographs 13 and 14, $\times 15 \times 140$; and 16 $\times 350$) and vitrain with cell structure, telain (photographs 17 and 18, $\times 70$). A. Roos.¹⁷

coal, composed very largely of the leaves of *Porodendron*. This is a brown coal of Lower Carboniferous (Mississippian) age.⁸⁰

The presence of algae is the diagnostic criterion for the identification of boghead cannel coal. These coals have a very limited distribution, but, inasmuch as the forms preserved in the coal represent complete plant structures, systematic studies have been made of the algae of a few classical regions such as the boghead (torbanite) region of Scotland⁸¹ and that of Autun,⁸² France.

Fungi are represented in coal, particularly by the bodies called sclerotia. These have been studied and described by Stach.⁴⁷ There appears to be no question of the occurrence of sclerotia in brown-coal (Fig. 18) but some uncertainty exists about the correctness of the identification of certain forms observed in polished-and-etched surfaces of bituminous coals (Fig. 19).

Resin bodies and waxes found in coal do not possess organic structure but consist of secretory or excretory masses. When they exist as rodlets (Fig. 20) they presumably have an external form representing the impression of the cell in which the secretion took place. In thin sections, probably representing wood tissue of primitive Gymnosperms (*Medullosa*), rodlets commonly appear as elliptical structureless bodies (Fig. 21). Waxes even more than resins are lacking in morphological structure, being mainly excretory in nature, commonly occurring in droplets embedded in the coal.

Opaque matter is a constituent of cer-

tain types of coals such as the splint coals of North America (Figs. 1 and 2) and probably also of most coals called durain

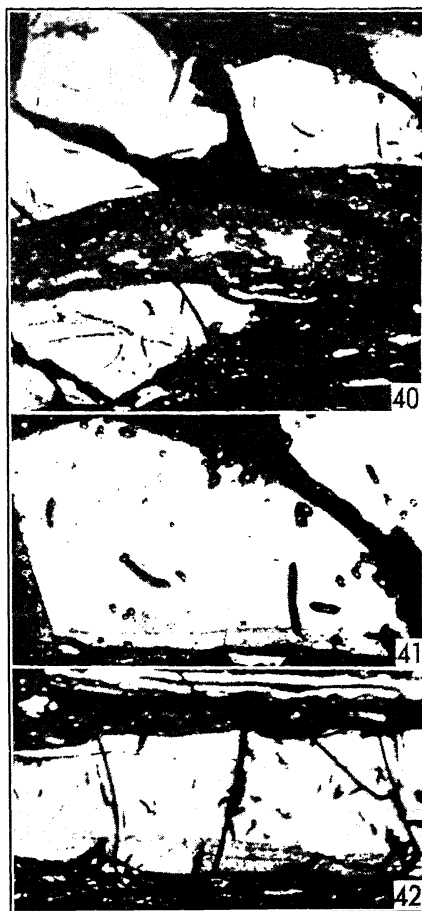


FIG. 16. According to Roos the illustrations numbered 40, 41, and 42 represent inclusions of pure collain in durain. "Energetic etching did not produce any traces of structure, as will be clearly shown by Fig. 41, which was taken at a higher magnification." (Photographs 40 and 42. $\times 70$; 41, $\times 140$.) After Roos.¹⁷

⁸⁰ Bode, H., and Feist, G., *Braunkohle*, 27, 1070-87 (1926).

⁸¹ Temperley, B. N., *Trans. Roy. Soc. Edinburgh*, (3) 58, 855-68 (1936).

⁸² Bertrand, C. E., *Bull. soc. ind. minérale*, (3) 6, 453-506 (1892).

or *matte* coals in Europe. The botanical significance of opaque matter has been the subject of much speculation and research by certain coal botanists and geologists,

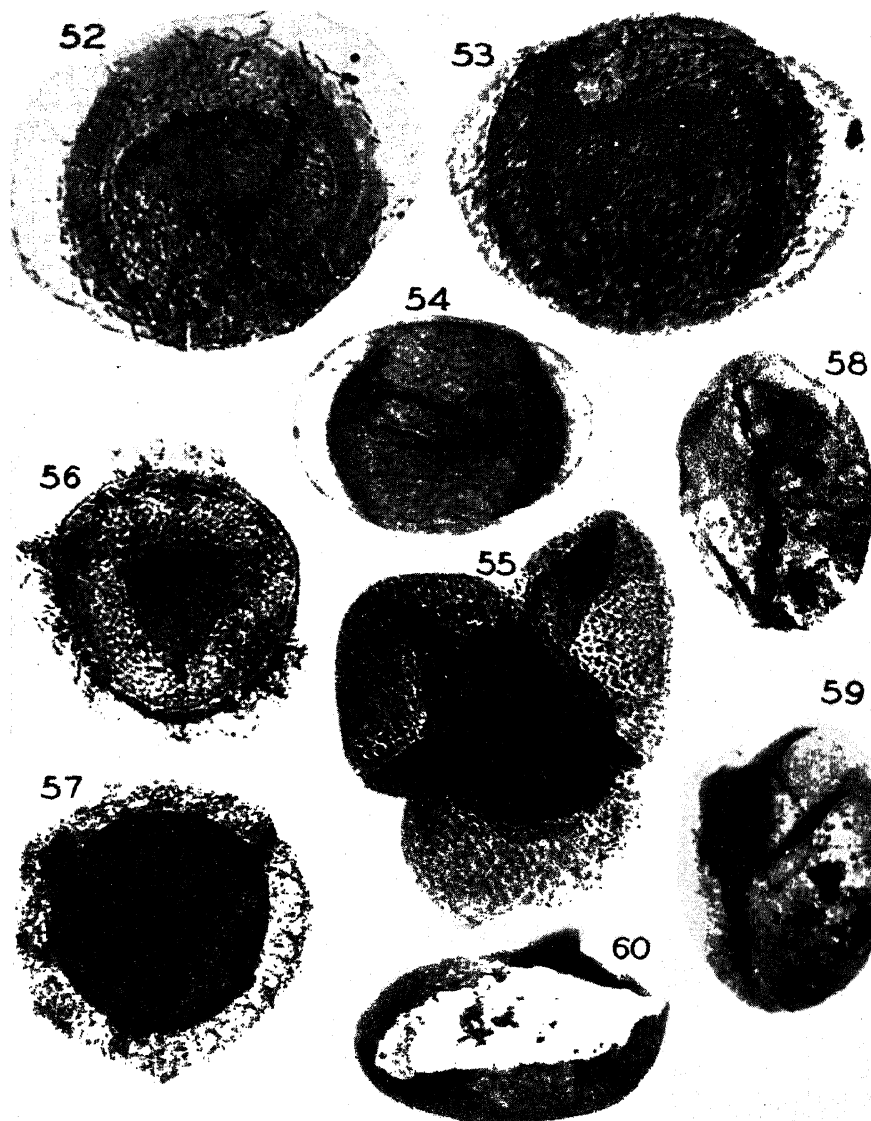


FIG. 17. A group of spores isolated by maceration from Herrin (No. 6) Seam or Co (No. 2) Seam coal in Illinois. Photographs by McCabe or Schopf.⁵⁴

No. 52 *Parasporites maccabei*
 No. 53 *Parasporites maccabei*
 No. 54 *Parasporites maccabei*
 No. 55 *Cystosporites breretonensis*
 No. 56 *Triletes triangulatus*

No. 57 *Triletes triangulatus*
 No. 58 *Sporites plicatus*
 No. 59 *Sporites plicatus*
 No. 60 *Sporites plicatus*

particularly Thiessen and Sprunk¹⁴ in America and Stach³³ in Germany.

Thiessen recognized two kinds of opaque matter: semitranslucent or brown matter, and finely divided or granular opaque matter. The brown matter is this color only in very thin sections. The granular

opaque matter, according to Thiessen and Sprunk, originates in and is due to the disintegration of the secondary wall of the tracheids of wood cells. It remains opaque, however thin the section is ground (Fig. 22).

Stach, as a result of the study of polished surfaces of durains, recognized three varieties of opaque substance, which he

³³ Stach, E., *Sitzber. preuss. geol. Landesanstalt*, No. 7, pp. 15-25, 1932.

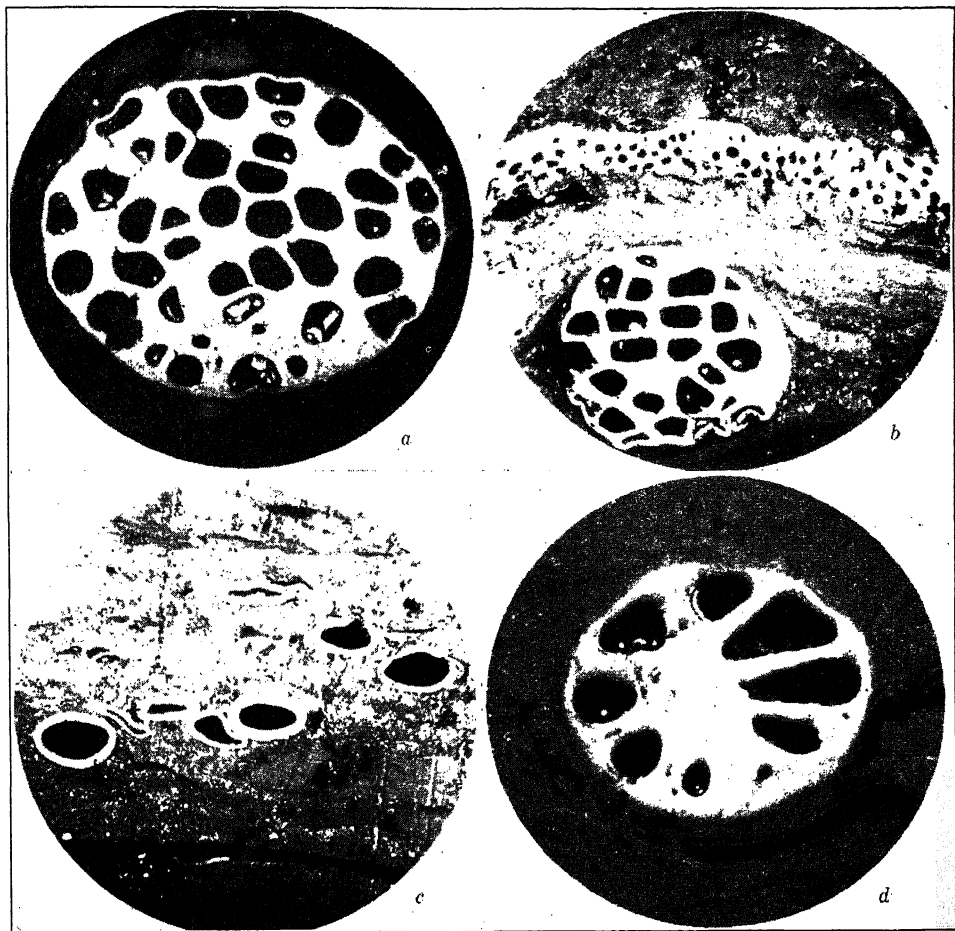


FIG. 18. Sclerotia from brown coals, after Stach.⁴⁷

a and b. *Sclerotites brandonianus* from Lower Mesozoic *Haribraunkohle*. ($\times 775$.)

c. *Sclerotites cavatoglobus* St. from Eocene *Haribraunkohle* from Dorog, Hungary. ($\times 775$.)

d. *Sclerotites* sp. from Tertiary coal from Canca-Philadelphia Columbia. ($\times 1550$.)

designated particles, flakes, and granules. The opaque granules appeared to correspond to the granular opaque matter of Thiessen and Sprunk, but Stach did not explain their origin, although he expressed the opinion that they were in some way related to microspores. The opaque particles and opaque flakes appeared to con-

sist mainly of small particles of fusain or sclerotia fragments. Stach placed no diagnostic significance on the occurrence of opaque matter in durain.

The difference between fusain and granular opaque matter is probably a matter mainly of academic interest, since both materials appear to be highly carbonized

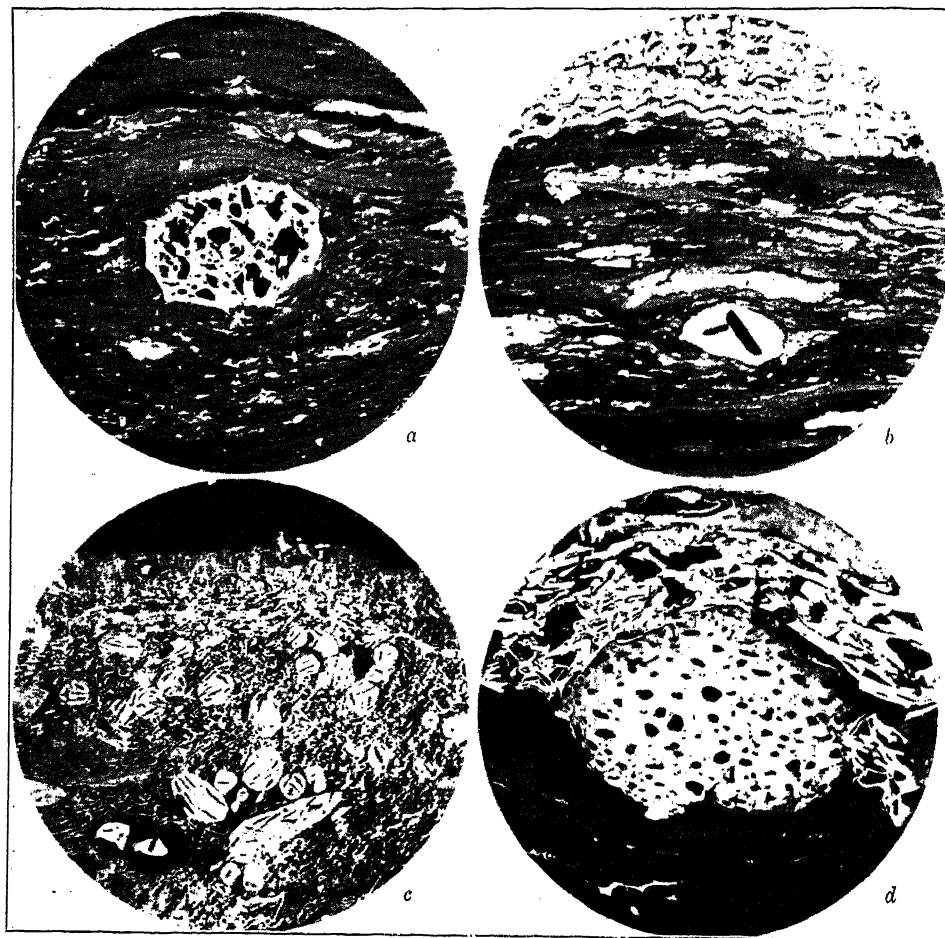


FIG. 19. Forms in bituminous coal identified as sclerotia by Stach.⁴⁷

a. A sclerotium in durain of *Flammkohle* from the Ruhr. ($\times 155$.)

b. A sclerotium (*Kerbensklerotium*) in a durain from *Gasflammkohle*. ($\times 155$.)

c. Sclerotia (*Kerbensklerotia*) in a Sarre coal. ($\times 155$.)

d. Deformation of fusain by a sclerotium (*Flammkohle*) from the Ruhr. ($\times 155$.)

as indicated by their opacity in the thinnest possible section and their brilliance in polished sections.

Investigations by Thiessen¹⁴ and by Hickling and Marshall^{18, 84} have demonstrated that the vitrain bands in bituminous coals in this country and in England are composed of identifiable wood. Thiessen and Sprunk⁸⁵ have said:

84 Hickling, H. G. A., and Marshall, C. E., *Trans. Inst. Mining Engrs. (London)*, **84**, 13-23, (1932-3).

85 Thiessen, R., and Sprunk, C. G., *U. S. Bur. Mines, Tech. Paper* **564**, 3 (1935).

The remaining plant structures in the anthraxylon strands are of specific types represented by definite structures, one assigned to the genus *Bothrodendron* [sic] [Fig. 23] and the other to the genus *Sigillaria*. The gymnosperms are also represented by two definite types, one a cycadophyte [Fig. 24] and the other a conifer [Fig. 25].

As a result of the careful studies that have been made of the characteristics of the structure of vitrain and the correlation of the structure with impression fossils, it is apparent that vitrain has its value as paleontological material.



FIG. 20. Resinous casts exposed on a slab of Herrin (No. 6) Seam coal from mine at Zeigler, Ill. Photograph by L. D. Vaughan, courtesy Illinois State Geological Survey. ($\times 6\frac{1}{2}$.)

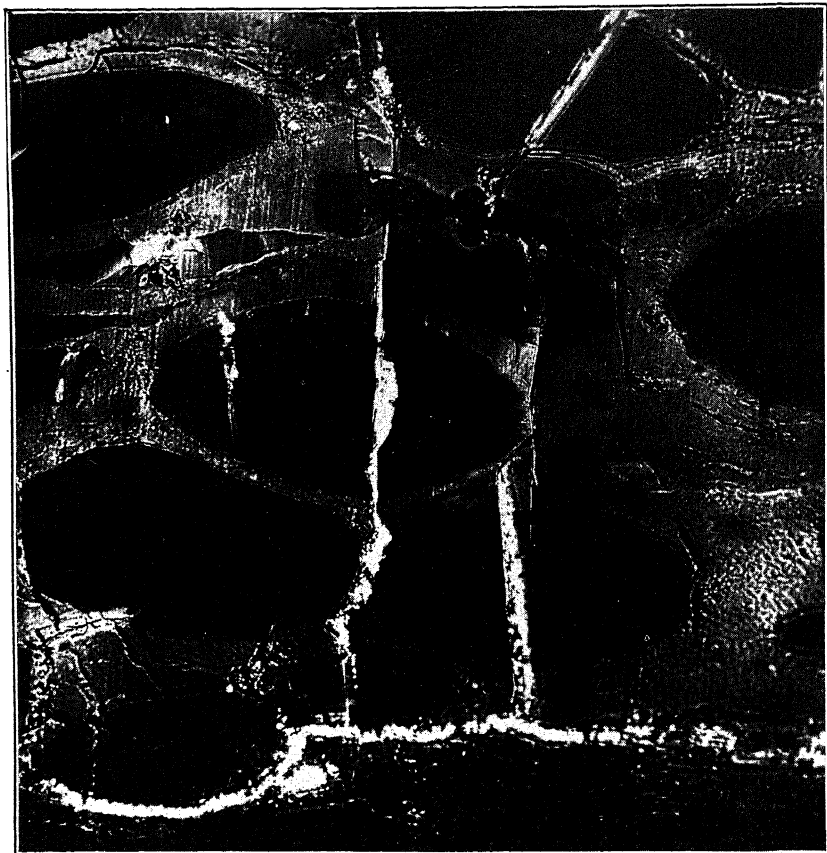


FIG. 21. Elliptical resin rods in a band of vitrain in Illinois high-volatile bituminous coal. Photograph by L. C. McCabe. ($\times 200$.)

PRACTICAL APPLICATION OF COAL PETROGRAPHY

COAL PREPARATION AND UTILIZATION

The practical significance of coal petrography up to this time has been mainly in the field of coal preparation. Just as the petrographic constitution of a coal provides a fundamental basis for type classification, it also provides a basis for controlling the nature of the coal composition mechanically. It is quite possible, by taking advantage of the differences that exist

in the physical properties of the different components of coal, so to adjust the procedure of mechanical preparation that concentrations of certain constituents can be brought about, thus producing a type of coal having characteristics quite different from the average quality of the coal in the bed. Such possibilities provide a means for preparing from common banded coal several types of coal, one or more of which may be better adapted for some specific use, such as combustion in household stokers or for use in coking or briquetting,

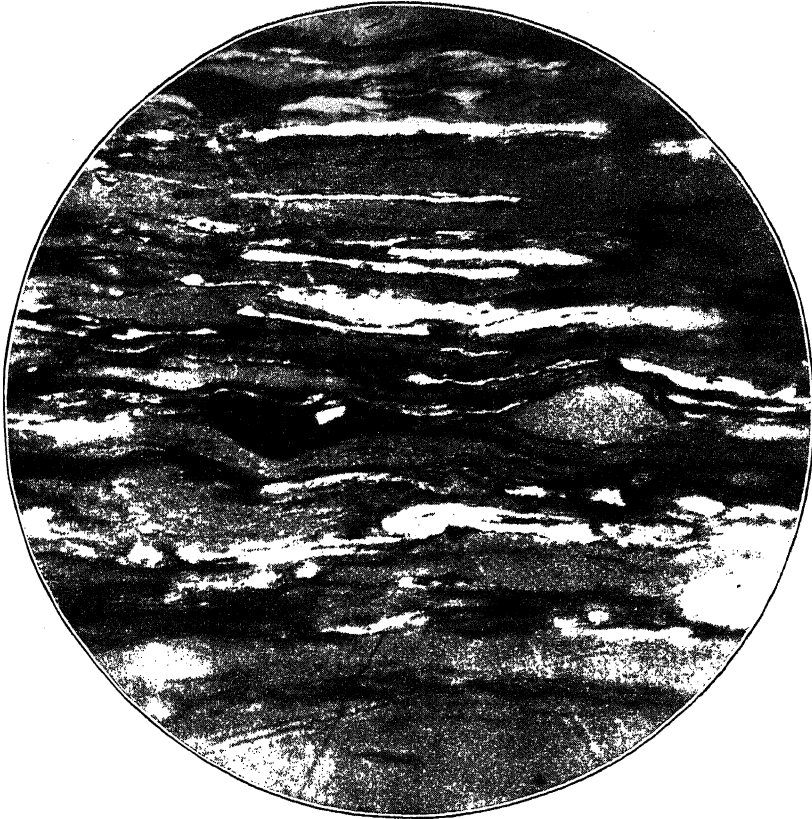


FIG. 22. Thin sections of the coal showing the nature of the granular opaque matter occurring in small black particles.⁸ This picture also shows thin-walled microspores found in this coal. Taggart Seam coal, Roda, Va. ($\times 1,000$.)

than the raw coal would be. From another point of view, a study of the coal produced under ordinary methods will usually reveal unsuspected variations in the characteristics of the fuel entering into the various sizes. An understanding of such variations is undoubtedly important to any coal producer who desires to maintain a standard product and to understand the characteristics of his coal as produced.

For a number of years at different places in Europe and America, more or less individual interest has been taken in the appli-

cation of coal petrography to coal preparation and utilization. Lomax⁸⁶ called attention to the importance of a knowledge of the constitution of coal in controlling spontaneous combustion. His investigations of the microscopic characteristics of coal were stimulated by this interest.

During the third decade of the century, in the years shortly after the announcement of the Stopes' petrographic terminology, the significance of petrographic vari-

⁸⁶ Lomax, J., *Trans. Inst. Mining Engrs. (London)*, 46, 592-635 (1913-4).

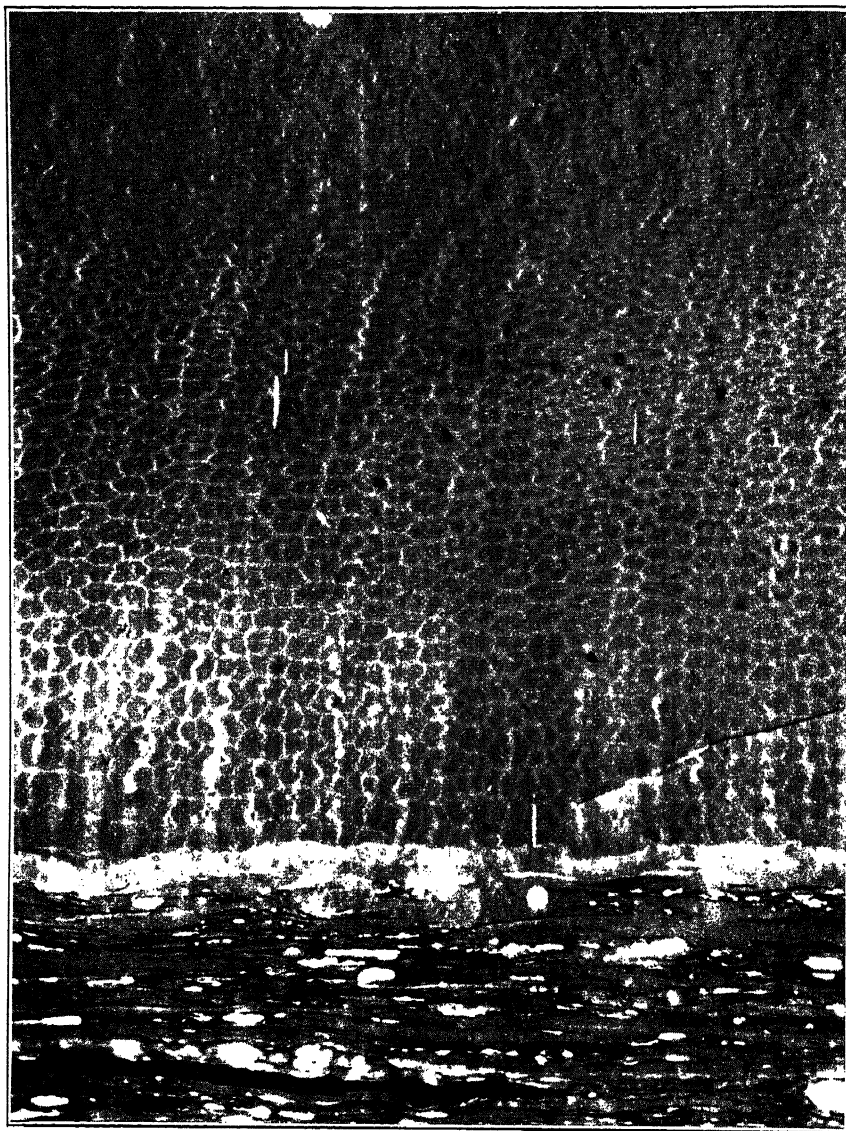


FIG. 23. "Thin cross section of coal from upper part of lower bench of the Freeport coal. This shows a transverse section of the predominant lycopod structure, probably the outer part of the bark of a *Bothredendron* [*sic*]. There is a first zone in which the cell structure is almost effaced; upon this follows a zone of peculiar well-preserved fibers. Inwardly the structure becomes poorer in preservation in a third zone of fibers." ($\times 200$.) After Thiessen and Sprunk.⁵⁵

ability of coal with respect to preparation and utilization came to be recognized. In 1923, Stopes and Wheeler⁸⁷ discussed the characteristics of the banded ingredients with respect to distillation, coking tests,

hesion of particles. . . . Vitrain particles were well sintered on coking, but the consolidation of the mass was not so pronounced as with clarain. . . . The coke assumes a distinct 'mushroom' shape."

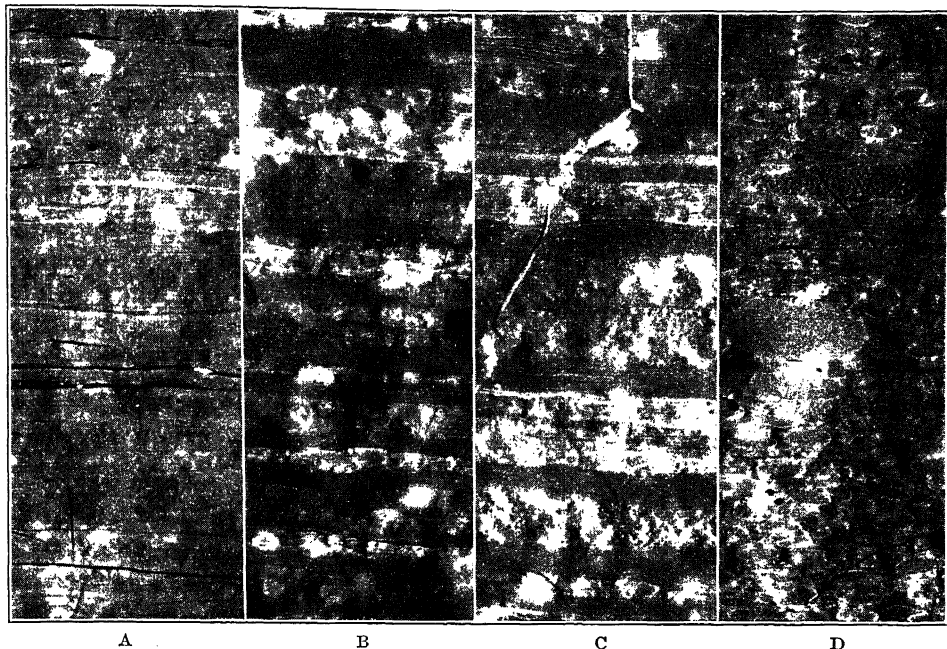


FIG. 24. A series of illustrations showing the structure of cycadophyte stem from the xylem to outer bark. ($\times 115$.)

A. Xylem: wood fibers with bordered pits, resins, and medullary rays indistinctly discernible.

B. A zone in which resinous tissue alternates with fibrous tissue.

C. The resinous tissues alternate with fibrous tissues and have broadened.

D. Outer bark: The resinous tissues have increased in thickness to such an extent that all is highly resinous. The cell walls have decomposed, and hardly anything by resin remains. After Thiessen and Sprunk.⁸⁸

etc. Referring to previous work by Lessing,⁸⁸ they stated that "durain underwent no change in form during coking." The particles retained their angular shape and showed little tendency to cohere. "Clarain showed considerable fusion and co-

A study of the coking characteristics of banded ingredients of the Campine coals, France, by de Booseré⁸⁹ resulted in one of the early contributions to the literature of this subject. De Booseré found it possible to separate vitrain, durain, and fusain. Clarain, being a mixture of different components, was impossible to differen-

⁸⁷ Stopes, M. C., and Wheeler, R. V., *Fuel*, **2**, 29-41, 83-92, 122-32 (1923).

⁸⁸ Lessing, R., *Trans. Chem. Soc.*, **117**, 247-56 (1920).

⁸⁹ De Booseré, O., *Ann. mines Belg.*, **27**, 369-96 (1926); *Fuel*, **5**, 522-7 (1926).

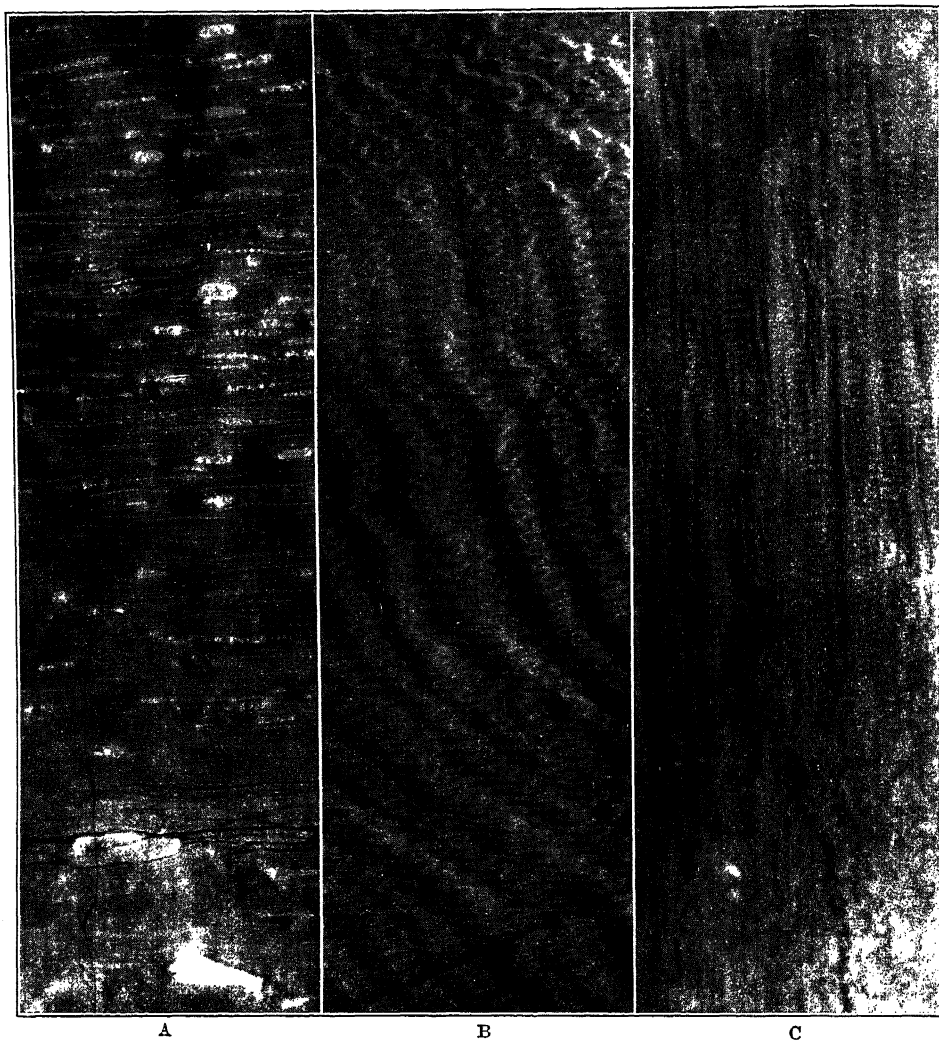


FIG. 25. A. Thin cross-section of a band of anthraxylon (vitrain) showing a tangential section of coalified coniferous wood, with medullary rays on the tangential surface and cross-sections of bordered pits in the radial walls. ($\times 200$.) After Thiessen.¹⁴

B. Thin cross-section of a band of anthraxylon composed of the outer cortex of a lycophyte. After Thiessen.¹⁴

C. "Thin horizontal section of Upper Freeport coal, lower bench. This is a typical illustration of the Cycadophyte structure seen over and over again in horizontal sections, showing characteristic slotlike bordered pits. In many cases this structure is seen associated with characteristic rodlets or with parts of a stem having alternate zones of resinous parenchyma and woody fibers." ($\times 200$.) After Thiessen and Sprunk.⁸⁵

tiate definitely. An illustration was given of the coke buttons made from whole coal and the three ingredients used, the characteristics of the buttons corresponding in all respects to those obtained by later investigators; the illustration shows that the vitrain coke had expanded more than the cokes from the whole coal or the clarain, and that the durain or fusain did not swell at all. Vitrain yielded the greatest proportion of extractible materials.

Vitrain yields more tar and more volatile matter in general, than the other fractions, has a much higher agglutinating value and a higher swelling index, probably related to its high content of extractible material. The coke from vitrain is always more swollen than that of the coal from which it has been separated. It appears that it is to this fraction that bituminous coal mainly owes its swelling and caking properties. By mixing vitrain with non-caking coal a normal coke may be obtained. Durain, on the other hand, has a lower agglutinating value than the original coal, and does not swell appreciably. Although of low caking power, the durains examined coked well but the cokes obtained were dry and full of cracks. These faults disappear when the durain is coked in admixture with the corresponding vitrain. Fusain behaves as an inert material during coking.⁹⁰

These statements have been substantiated repeatedly by other investigators, with applications to individual coals; they represent the general status of information in regard to the behavior of the banded ingredients, specific studies making application to particular coal.^{64, 91}

⁹⁰ De Booseré, O., *Fuel*, **5**, 524 (1926).

⁹¹ Winter, H., *Glückauf*, **63**, 483-91 (1928). Hoffmann, E., *Jahrb. preuss. geol. Landesanstalt*, **51**, 253-308 (1930). Legraye, M., *Rev. universelle mines*, [8] **3**, 38-40 (1930); *Les constituents des charbons, leur influence sur quelques propriétés industrielles*, Dunod, Paris, 1934, 152 pp. Lehmann, K., and Stach, E., *Glückauf*, **66**, 289-99 (1930). Lehmann, K., *Proc. Third In*

The adaptability of the various banded ingredients to combustion in underfeed domestic stokers has been under investigation by McCabe,⁹² who reported better results obtained from Illinois coals containing a small amount of vitrain than from those containing a relatively large amount.

Because of the evidence produced, that control of the proportion of the banded ingredients of coal is important, considerable attention has been given to a determination of the effect of preparation processes upon the type of the produced coal as determined by its petrographic composition. Hoffmann has investigated the methods of separating and concentrating of banded ingredients as reported in 1930.⁹³ Stach⁹⁴ and his associates perfected a method of studying fine sizes of Ruhr coal for the purposes of petrographic analysis, using dust mounted in wax and polished. Such investigations greatly stimulated the interest in coal petrography in Europe, particularly on the continent, and resulted in several textbooks on the subject beside Stach's *Lehrbuch*.^{1, 95}

tern. Bituminous Coal Conf., **2**, 679-700 (1931). Strevens, J. L., *Colliery Guardian*, **142**, 572-6, 667-8 (1931); *Gas J.*, **193**, 583-5, 655-7 (1931). Lehmann, K., and Hoffmann, E., *Brennstoff-Chem.*, **13**, 181-7 (1932). Maier, L. M., and Zyckermann, L. E., *Koks i Khim.*, **3**, 51-62 (1933). Wang, C. C., *Bull. Geol. Soc. China*, **12**, 413-32 (1933). Boley, C. C., and McCabe, L. C., *Trans. Illinois State Acad. Sci.*, **29** (2), 153-5 (1936). Pieters, H. J. A., Koopmans, H., and Hovers, J., *Fuel*, **15**, 43-7 (1936). Kühlwein, F. L., *Tech. Mitt. Essen*, **30**, 308-18 (1937). McCabe, L. C., *Mining Congr. J.*, **23**, 18-9 (1937). Thiessen, G., *Illinois State Geol. Surv., Bull.* **64**, 1937, pp. 115-6.

⁹² McCabe, L. C., *Mech. Eng.*, **60**, 217-21 (1938).

⁹³ Hoffmann, E., *Jahrb. preuss. geol. Landesanstalt*, **51**, 268 (1930).

⁹⁴ See pp. 227-56 of ref. 47.

⁹⁵ Potonié, R., *Einführung in die allgemeine Kohlenpetrographie*, Gebrüder Borntraeger, Berlin, 1924, 285 pp. Dolch, M., *Brennstofftechnisches Praktikum*, Knapp, Halle, 1931, 148 pp.

The petrographic analysis of screenings of a representative group of Illinois coals has been reported by McCabe,⁹⁶ seams 2, 5, and 6 being represented in the investigation, but most of the determinations being made on the Herrin (No. 6) Seam coal. An example is given showing that, for one coal in which the proportion of vitrain in the seam is about 20 percent, in the 1.25 by 0.75 inch coal it is about 42 percent, and in the minus 48-mesh coal it is 79.3 percent.

Sufficiently extended studies have been made by McCabe and associates to indicate that the proportion of vitrain generally increases in the order indicated in the natural fine sizes of Illinois coals, and that in sizes less than minus 48 mesh the fusain generally shows great increase, exceeding the vitrain in amount in minus 100-mesh sizes.⁹⁷

Broche and Nedelmann⁹⁸ reported an investigation of the influence of the banded ingredients on briquetting of coals with a binder. Fusain was the ingredient which was considered particularly detrimental because of its dust-producing property. Pier-sol⁶¹ after investigating briquetting without a binder reported that

Coal in which the ingredients occur in their natural proportions is more favorable for the formation of briquets than any blend which greatly increases the percentage of either vitrain or fusain. Clarain makes as good briquets as the whole coal, probably because its constitution closely approximates that of the whole coal, and in clarain the ingredients are intimately blended.

Such examples that have been given and references cited indicate the practical significance of coal petrography and utilization. The development of petrographic

technique depends very largely upon the expansion of selective, discriminating utilization of the banded coals. Possibly, when it is realized that the processes of coal preparation can be readily adjusted so that segregation and concentration of coals of special petrographic composition, and hence of special chemical constitution, are possible, the significance of such a possibility will be given more systematic attention by chemists and engineers.

COAL DESCRIPTION

One important aspect of coal petrography is the promise it holds for an improved technique of description and classification of coals. The kind, distribution, and quantity of petrographic components composing a coal are items essential to an understandable description of a coal. It is of primary importance that agreement be reached concerning the petrographic names and their meaning.⁹⁹ The widespread use of the terms vitrain, clarain, durain, and fusain in other parts of the world than North America makes their general use in America desirable, and all the more because the names are in accordance with petrographic terminology and have petrographic rather than genetic or paleobotanical significance. There is the further advantage that these names are primarily based upon megascopic rather than microscopic considerations and, hence, are readily applied without reference to microscopic criteria.

Many coals have been described in petrographic terms. The most comprehensive application of this method is that of the Bureau of Mines in describing the coals investigated in cooperation with the American Gas Association to determine gas-,

⁹⁶ McCabe, L. C., *Trans. Am. Inst. Mining Met. Engrs.*, **119**, 321-9 (1936).

⁹⁷ Personal communication.

⁹⁸ Broche, H., and Nedelmann, H., *Glückauf*, **70**, 979-90 (1934).

⁹⁹ Cady, G. H., *Econ. Geol.*, **34** (5), 475-94 (1939).

coke-, and byproduct-making properties (see Chapter 22).

The profile method of description of American coals in terms of petrographic constituents has been followed by European technologists in more or less modified form generally employing the Stopes terminology or the Second Heerlen Conference modification of that terminology.³⁴ Kühlwein²⁵ used the method in describing a large number of Ruhr coals, also providing analyses of the seams and benches of coal in terms of the banded ingredients. The graphic representation of petrographic characteristics when used to delineate the petrographic variations by bench through the seam often provides a basis for correlations because of similarity in the distribution of petrographic characteristics within the seam over considerable areas. This was illustrated by Koopmans,⁶⁵ who by reference to seven profiles of one seam and five of another showed the usefulness of the profile method in demonstrating the persistent physical variations in the coal seams.

Roos¹⁰⁰ (1935) presented a series of twenty profile sections of a single coal seam in the Limburg field of the Netherlands. The general persistence of similar petrographic characteristics of the coal was claimed on the basis of the similarity of the profiles.

In the numerous reports of the British Department of Scientific and Industrial Research⁶⁸ concerned with the physical

and chemical survey of the national coal resources of the different coal fields, many profiles of coal seams have been presented based upon the microscopic examination of coal columns. In these profiles, bright (vitrain and clarain), dull (durain), inter-banded bright and dull, fusain and inferior coal have been recognized and also inter-bedded mineral matter.

A detailed profile of the Otto coal seam of Upper Silesia was prepared by Drath.¹⁰¹ The profile showed graphically the proportionate amounts of fusinite, semifusinite, telinite, collinite, exinite, resinite, micro-nite (opaque matter), and pyrite present in each 20 millimeters of the coal bed as determined by microscopic examination of polished blocks taken from a column of the coal seam. Profile studies were also made of the Sattelfözü-Niederbank coal of the Polish coal basin.¹⁰²

Although profiles based upon microscopic determinations are undoubtedly important for an understanding of the nature and distribution of variations in a coal seam, they are expensive because of the time consumed in making thin sections or polished surfaces and in the microscopic examination. Profiles based upon megascopic determinations are probably all that can be hoped for generally, but such profiles should at least be expected as the minimum requirement of technical description of a coal seam.

¹⁰¹ See pp. 685-770 of ref. 62.

¹⁰⁰ See pp. 1057-161, especially p. 1133, of ref. 17.

¹⁰² Doktorowicz-Hrebniński, St., *Surv. Geol. Pologne, Bull. 8*, 209-94 (1937).

CHAPTER 4

CALORIFIC VALUE OF COAL *

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GROSS AND NET CALORIFIC VALUES

As the calorific value test is a direct measure of the energy value of a coal it is the most significant of all the laboratory tests made in coal analysis for determining the value of coal as a fuel. Calorific values as determined and reported are gross calorific values. A correction is sometimes made for differences between the laboratory conditions and those occurring in burning coal as fuel, and such corrected values are designated as net calorific values.

Definitions of gross calorific value and of net calorific value as adopted in tentative form by the American Society for Testing Materials¹ are as follows:

Gross Calorific Value, H_g . In the case of solid fuels and liquid fuels of low volatility, the heat produced by combustion of unit quantity, at constant volume, in an oxygen bomb calorimeter under specified conditions.

Note. The conditions are initial oxygen pressure of 20 to 40 atmospheres, final temperature of 68 to 95° F (20 to 35° C), products in form of ash, liquid water, and gaseous CO₂, SO₂, and nitrogen. This definition is not applied to gaseous or highly volatile liquid fuels.

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¹ *ASTM Standards*, Pt. III, 1939, p. 585.

Net Calorific Value, H_i . In the case of solid fuels and liquid fuels of low volatility, a lower value calculated from the gross calorific value as the heat produced by combustion of unit quantity, at constant atmospheric pressure, under conditions such that all water in the products remains in the form of vapor.

Note. The net calorific value is calculated from the gross calorific value by making a deduction of 1,020 Btu per pound (567 calories per gram) of water derived from unit quantity of fuel, including both the water originally present as moisture and that formed by combustion. The deduction is not equal to the latent heat of vaporization of water (1,050 Btu per pound at 75° F (24° C) because the calculation is made to reduce from gross value at constant volume to net value at constant pressure, for which the correct factor is 1,020 Btu per pound.

The symbols H_g and H_i are used in these definitions in an attempt to get agreement with standardizing bodies of other countries in the designation of the two values. The H designates heat, and the subscripts s and i are from the French words *supérieur* meaning higher and *inférieur* meaning lower.

In the metric system, the unit of fuel is 1 gram and the heat unit is the calorie, which is the quantity of heat necessary

to raise the temperature of 1 gram of water 1° C at 15° C. This is the 15° calorie commonly used in this country for thermochemical work. To be exact, the temperature of the water is specified because of a slight difference in specific heat of water at various temperatures.

In the English system the unit quantity of fuel is 1 pound and the standard heat unit is the British thermal unit, or Btu, which is the quantity of heat required to raise the temperature of 1 pound of water 1° F. Calorific values expressed in calories per gram may be converted into Btu per pound by multiplying by 1.8, the ratio between the Centigrade and Fahrenheit degree.

In the calorific-value determination as made in the laboratory the products of combustion are cooled to the temperature of the calorimeter, which is 68 to 95° F, the water vapor formed during combustion being condensed to liquid water. This is the gross calorific value; it is used in reporting coal analyses and in comparing different coals. Unless otherwise designated, it is the value referred to throughout this chapter.

In the burning of coal as fuel, conditions exist other than those that prevail in the laboratory determination of calorific value, because the water vapor formed during combustion in a furnace is not condensed to liquid water but remains in the form of vapor. Also, the fuel is burned not under conditions of constant volume but under conditions of constant atmospheric pressure. According to the definition, net calorific value may be calculated from the determined gross value, as follows:

Net calorific value in Btu per lb (H_i) =

Gross calorific value (H_g) -

$$\frac{1,020 \times \text{Percentage total hydrogen} \times 9}{100}$$

Since the calculation of net calorific value requires a hydrogen determination as well as a calorific-value determination, coals usually are compared on the basis of gross calorific values even though the latent heat of the water vapor is lost in the burning of the fuel. Ordinarily in the purchase of coals on the basis of calorific values the competing coals have about the same hydrogen content, and so the correction for the amount of heat lost in the water vapor is virtually constant.

In comparing bituminous coal, anthracite, petroleum, and coke, the net calorific values give a better comparison because of the considerable differences in hydrogen content. Because of the low hydrogen content of coke virtually all the heat of that fuel is available on burning, whereas as much as 6.4 percent of the gross heat of petroleum may remain in the uncondensed water vapor. Fieldner and Selvig² gave such comparisons for bituminous coal, anthracite, petroleum, and coke as shown in Table I. They constructed graphs from some 2,000 analyses of various coals to study the application of the hydrogen-volatile matter ratio in calculating net heating value. The graphs show that the hydrogen contents of high-volatile bituminous coal, low- and medium-volatile bituminous coal, and anthracite may be estimated from their volatile-matter contents within 0.6 percent. For subbituminous coals and lignite they found that the differences between estimated hydrogen content and actual hydrogen content are within 0.8 percent, but if these coals are weathered the error may approach 1 percent. The conclusion from this study is that, for most coals, the hydrogen can be estimated if the volatile matter is known, and that this estimation is sufficiently close so that any

² Fieldner, A. C., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper 197* (1918), 11 pp.

error in the calculated net calorific value will not exceed 0.5 percent of the value calculated from the actual hydrogen content as determined by analysis.

TABLE I

HYDROGEN CONTENTS AND CALORIFIC VALUES OF FOUR FUELS²

Kind of Fuel	Hydrogen percent	Gross Calorific Value Btu	Net Calorific Value Btu	Heat Lost in Water Vapor at 20° C percent
Bituminous coal	5.18	13,560	13,075	3.6
Anthracite	2.50	12,780	12,545	1.8
Petroleum	12.75	18,540	17,345	6.4
Coke	0.30	12,500	12,470	0.2

A study by Evans³ of some 750 analyses of representative British coals confirms this conclusion. The hydrogen content on the dry-coal basis was plotted against volatile matter, and a smooth curve was drawn through the average hydrogen values at 1 percent volatile matter intervals. The resulting curve showed that 99 percent of the individual hydrogen determinations were within ± 0.5 percent of the average value, which corresponds to a maximum error in the net calorific-value correction of 26 calories.

LABORATORY METHODS FOR DETERMINATION OF CALORIFIC VALUE

HISTORICAL

Several types of calorimeters and methods for the determination of calorific value of coal were introduced during the latter part of the nineteenth century, and for each method some special advantage was claimed. Several of these methods which have been described by Parr⁴ can be grouped as follows:

³ Evans, T., *Analyst*, **65**, 352-3 (1940); *Fuel*, **19**, 181-2 (1940).

⁴ Parr, S. W., *The Analysis of Fuel, Gas, Water, and Lubricants*, McGraw-Hill Book Company, New York, 4th ed., 1932, p. 221.

Measurement of Reducing Power of Coal.

In this method, introduced in 1843 by Berthier, the reducing power of coal was measured by heating 1 gram of coal with litharge and multiplying the weight of the lead button obtained by a factor. The product represents theoretically the reducing power of the carbon in terms of Btu. As tests have shown that the results may be considerably in error, the method has historical rather than practical interest.

Combustion by a Solid Oxidizing Agent.

In the Lewis Thompson calorimeter the coal sample was mixed with potassium nitrate and potassium chlorate. This mixture was charged into a cartridge and ignited by a fuse, covered immediately by a copper bell, and immersed in water to measure the heat produced. According to Scheurer-Kestner⁵ this apparatus normally gave results that were in error by about 15 percent.

The Parr sodium peroxide calorimeter, described later, and an English modification called the Roland Wild calorimeter⁶ have been used extensively for technical work. Sodium peroxide is used in both these methods as the oxidizing agent. As it absorbs the gaseous products of combustion, no provision is necessary for the release of gas pressure.

Combustion in a Stream of Oxygen at Constant Pressure. The best-known calorimeters of this type were those developed by Thomson,⁷ Fischer,⁸ Carpenter,⁹ and

⁵ Scheurer-Kestner, M., *Bull. soc. ind. Mulhouse*, **54**, 506-13 (1888); *J. Soc. Chem. Ind.*, **7**, 868-9 (1888).

⁶ Sinnatt, F. S., *Coal and Allied Subjects*, H. F. and G. Witherby, London, 1921, pp. 190-2.

⁷ Thomson, W., *J. Soc. Chem. Ind.*, **5**, 581-4 (1886).

⁸ Fischer, F., *Dinglers Polytech. J.*, **258**, 330; *J. Soc. Chem. Ind.*, **5**, 159 (1886).

⁹ Carpenter, R. C., *Trans. Am. Soc. Mech. Engrs.*, **16**, 1040-56 (1895).

Darling.¹⁰ With these calorimeters a current of oxygen was conducted through a chamber where the fuel was burned at constant pressure. The chief disadvantage of this type is the likelihood of incomplete combustion, especially with high-ash coals.

Combustion in a Bomb with Oxygen under Pressure at Constant Volume. The first calorimeter of this type was devised by Berthelot¹¹ in 1881. As the accuracy of the oxygen-bomb calorimeter for measuring the calorific value of coal became established,¹² improvements were made in the construction and operation of such calorimeters so that now this type is the most accurate of any that have been used in coal calorimetry. Among the successful modifications are those of Mahler,¹³ Atwater,¹⁴ Emerson,¹⁵ and Parr.¹⁶

In 1903, Brame and Cowan¹⁷ selected the Lewis Thompson, William Thomson, Fischer, and Mahler calorimeters as representative types for study. With the exception of Parr's sodium peroxide calorimeter this selection covered the various types mentioned. This investigation showed that the experimental error is large with the first three methods, but with the oxygen-bomb method the greatest difference between any two results for the same coal

was 26 calories. The average results by these methods on five coals, summarized in Table II, show large variations when compared with Mahler's bomb method. A similar investigation was reported later by Gray and Robertson¹⁸ confirming the conclusion that the oxygen-bomb calorimeter has marked superiority over the other types.

TABLE II

SUMMARY OF AVERAGE RESULTS FOR CALORIFIC VALUE OF COAL BY REPRESENTATIVE TYPES OF CALORIMETERS,¹⁷—CALORIES PER GRAM

Coal	Type of Calorimeter			
	Potassium Chlorate and Nitrate Mixture, Lewis Thompson	Combustion in Stream of Oxygen		Oxygen Bomb, Mahler
		Wm. Thomson	Fischer	
A	8,418	8,284	8,139	8,629
B	7,235	7,178	7,509	7,713
C	8,331	8,324	8,243	8,617
D	8,144	8,233	8,050	8,395
E	8,178	7,882	7,627	8,027

OXYGEN-BOMB METHOD

The oxygen-bomb method as standardized by the American Society for Testing Materials¹⁹ is used by virtually all laboratories in this country. Oxygen-bomb methods are also accepted as standard in laboratories of other countries.²⁰

Precision in the determination of calorific value of coal by the oxygen-bomb method depends on (1) accurate thermometry to measure the heat retained by the calorime-

¹⁸ Gray, T., and Robertson, J. G., *J. Soc. Chem. Ind.*, **23**, 704-7 (1904).

¹⁹ A.S.T.M. Standards, Part III, 1939, pp. 37-41.

²⁰ Fieldner, A. C., and Selvig, W. A., *Fuel*, **17**, 266-71 (1938).

¹⁰ Darling, C. R., *Engineering*, **1902**, 801; *J. Soc. Chem. Ind.*, **21**, 927-8 (1902).

¹¹ Berthelot, M., and Vieille, *Ann. chem. phys.*, **6**, 546-56 (1885); *J. Soc. Chem. Ind.*, **5**, 159 (1886).

¹² Scheurer-Kestner, M., *Compt. rend.*, **112**, 233-6 (1891); *J. Soc. Chem. Ind.*, **10**, 659 (1891). Scheurer-Kestner, M., and Meunier-Dollfus, *Bull. soc. ind. Mulhouse*, **57**, 577-89 (1891); *J. Soc. Chem. Ind.*, **11**, 339 (1892).

¹³ Mahler, P., *Chem. Zentr.*, **63**, 889 (1892); *Bull. soc. encour. ind. nat.*, **91**, 317 (1892).

¹⁴ Atwater, W. O., and Snell, J. F., *J. Am. Chem. Soc.*, **25**, 659-99 (1903).

¹⁵ Emerson, C. J., *Ind. Eng. Chem.*, **1**, 17-8 (1909).

¹⁶ Parr, S. W., *8th Internat. Congr. Applied Chem.*, **1**, 389-93 (1912).

¹⁷ Brame, J. S. S., and Cowan, W. A., *J. Soc. Chem. Ind.*, **22**, 1230-33 (1903).

ter water, and (2) accurate knowledge and control of the heat lost from the system. The various factors affecting calorimetry have been discussed in considerable detail by White.²¹

A 1-gram sample of the coal is completely burned in a bomb filled with oxygen under pressure of 20 to 30 atmospheres. The bomb is immersed in a weighed quantity of water, and the heat developed by the burning of the coal is determined by measuring accurately the rise in temperature of the water surrounding the bomb. A cooling correction²² is applied to this temperature rise to correct for the small amount of heat lost to the surroundings by the calorimeter water. Corrections are also made for the heat of formation of nitric acid and aqueous sulfuric acid formed by oxidation²³ of the nitrogen of the coal, the nitrogen of the air in the bomb, and the sulfur of the coal. These acids are formed when coal is burned in an atmosphere of oxygen under high pressure. During the ordinary combustion of coal for fuel use the sulfur in coal burns to sulfur dioxide, which has a lower heat of formation than aqueous sulfuric acid. The application of these corrections in coal calorimetry is described in detail in *Technical Paper 8* of the Bureau of Mines.²⁴

In a calorimeter installation described by Davis and Wallace²⁵ the factors that

influence the cooling correction are controlled by surrounding the calorimeter with a complete water jacket maintained at constant temperature, and by providing the calorimeter with a constant-speed stirrer and a water seal to prevent evaporation. By this control a constant form of the temperature-rise curve is obtained and the cooling correction is obtained from a calibration curve. This simplifies considerably the calorimetric procedure by eliminating the calculation of cooling corrections for individual determinations.

The adiabatic calorimeter in which no heat is lost to the surroundings has been applied to the determination of calorific value to avoid the cooling correction. By this method the calorimeter is surrounded by a jacket through which water is circulated under close temperature control to correspond with the rise in temperature of the calorimeter water. Several methods of heating have been used to secure exact control of the jacket water temperature. These methods are of the following types: (1) chemical action,²⁶ where an acid solution is added from a buret to a basic solution in the calorimeter jacket; (2) electrical heating;²⁷ and (3) addition of hot or cold water through manually controlled valves.²⁸

The vacuum-jacketed calorimeter,²⁹ based on the principle of the Dewar flask, has not proved to be satisfactory for the determination of the calorific value of coal. When treated as adiabatic with no correc-

²¹ White, W. P., *The Modern Calorimeter*, Reinhold Publishing Corp., New York, 1928, 194 pp.

²² Dickinson, H. C., *Bull. Natl. Bur. Standards*, **11**, 189-257 (1915). Müller-Neuglück, H. H., *Angew. Chem.*, **49**, 180-5 (1936). Quass, F. W., *J. Chem. Met. Min. Soc. South Africa*, **38**, 413-35 (1938).

²³ Regester, S. H., *Ind. Eng. Chem.*, **6**, 812-22 (1914).

²⁴ Stanton, F. M., Fieldner, A. C., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper 8*, 30-2 (ed. of 1938) (1939).

²⁵ Davis, J. D., and Wallace, E. L., *U. S. Bur. Mines, Tech. Paper 91* (1918), 48 pp.

²⁶ Richards, T. W., Henderson, L. J., and Frevort, H. L., *Proc. Am. Acad.*, **42**, 573-93 (1907).

²⁷ Benedict, F. G., and Higgins, H. L., *J. Am. Chem. Soc.*, **32**, 461-7 (1910). Swietoslawski, W., and Pakovich, I., *J. Russ. Phys. Chem. Soc.*, **46**, 1284-93 (1914); *Chem. Abs.*, **9**, 2165 (1915).

²⁸ Gray, F. W., *Trans. Chem. Soc.*, **105**, 1010-4 (1914). Swietoslawski, W., *Rocz. Chem.*, **1**, 157-65 (1921); *J. Soc. Chem. Ind.*, **41**, 200A (1922).

²⁹ *Natl. Bur. Standards, Circ. 11*, 7, 3rd ed., 1917.

tion for thermal leakage an accuracy of the order of 0.5 percent is possible. If greater accuracy is desired, as in determining the calorific value of coal, a cooling correction becomes necessary, and the method offers no advantage over a well-designed water-jacketed calorimeter.

Because of the formation of nitric and sulfuric acids in oxygen-bomb calorimetry it is essential that the bombs have inner surfaces that are not attacked by these corrosive products of combustion. Platinum, porcelain enamel, and gold have proved suitable materials for lining the inner surfaces of the bombs. A very practical method that does away with troubles inherent in bomb linings is to make the entire bomb of an acid-resisting alloy such as that developed by Parr.³⁰ Such bombs have proved very satisfactory and are now used extensively. Nickel-lined bombs³¹ and Monel-metal bombs³² also have been used, but correction for the heat evolved through solution of the nickel lining or Monel metal is required. The application of this correction is difficult for coals high in sulfur.

In laboratories where a large number of determinations must be made every day, the use of electrical resistance thermometers and timing devices and the building of several calorimeter units into one installation^{25, 33} have been successful. Time is saved by operating two or more bombs simultaneously, and duplicate determinations can be made with different bombs.

³⁰ Parr, S. W., *J. Am. Chem. Soc.*, **37**, 2515-22 (1915).

³¹ Olin, H. L., and Wilkin, R. E., *Chem. & Met. Eng.*, **26**, 694-6 (1922). Stoppel, A. E., and Harding, E. P., *Ind. Eng. Chem.*, **20**, 1214-8 (1928).

³² Geniesse, J. C., and Soop, E. J., *Ind. Eng. Chem.*, **17**, 1197-9 (1925).

³³ Davis, J. D., and Cooper, H. M., *Ind. Eng. Chem.*, **16**, 579 (1924). Myers, C. A., Jr., *ibid.*, **10**, 1015-6 (1918). Vasser, H. S., *ibid.*, **11**, 467-8 (1919).

Occasionally a calorimeter may give erroneous results through a leak, faulty electrical insulation, binding of the stirrer, or some other common but not readily detected cause, but the chance is remote that two calorimeters will be out of order at the same time.

Calorimeters are best calibrated by means of standard samples of known calorific value as supplied by the National Bureau of Standards.³⁴ Such standard samples available are benzoic acid, naphthalene, and sucrose. Of these, benzoic acid is probably most used.

By adhering to the standard method of the American Society for Testing Materials¹⁹ and the use of standard samples for calibrating calorimeters, different laboratories should have no difficulty in obtaining close agreement when testing the same coal sample. The permissible difference for different laboratories in determinations made on duplicate samples of the same coal is 0.5 percent. The permissible difference between duplicate determinations made in the same laboratory is 0.3 percent. Usually, different laboratories have no difficulty in checking within these prescribed tolerances. These tolerances apply only when tests are made on duplicate portions of the same laboratory sample, which according to the standard procedure is coal pulverized to pass a No. 60 sieve.

SODIUM PEROXIDE BOMB

A rather ingenious type of calorimeter, which uses chemicals to supply the oxygen for combustion of the coal, is the Parr sodium peroxide calorimeter.³⁵ The coal is mixed with sodium peroxide (Na_2O_2)

I. Bur. Standards, Supplement to Circular C398 (1940), 11 pp.

³⁵ Parr, S. W., *J. Am. Chem. Soc.*, **22**, 646-52 (1900), **29**, 1606-22 (1907). Parr, S. W., and Wheeler, W. F., *Ind. Eng. Chem.*, **1**, 673-5 (1909).

and some potassium perchlorate (KClO_4) which acts as an accelerator to obtain complete combustion. The charge is ignited electrically in a bomb much smaller than that required in the oxygen-bomb method. The method is often used for so-called technical work. Since it does not have the fine accuracy of the oxygen-bomb method it is not accepted as a standard method in this country. Whatever popularity this method has is due chiefly to the relatively low cost of the apparatus and its ease of operation.

CALCULATION OF CALORIFIC VALUE FROM ANALYSIS

Various formulas have been devised and used for calculating calorific values from coal analyses. A number of these have been discussed critically by Jarrier³⁶ and by Veron.³⁷ Formulas based on the ultimate analysis are considered to be more reliable than those based on the proximate analysis.

Ultimate Analysis. Dulong's formula is probably the best known, and one form that has been used extensively is: Btu per pound = $14,544C + 62,028 \left(H - \frac{O}{8} \right) + 4,050S$.

In this formula, the oxygen of the coal is assumed to be associated with hydrogen in the proper ratio to form water, the excess hydrogen being available for combustion together with the carbon and sulfur. This excess hydrogen is sometimes designated as "available hydrogen."

Calorific values³⁸ as determined in the oxygen-bomb calorimeter are usually within 1.5 percent of values calculated by Dulong's formula, for anthracitic, semianthra-

citic, and bituminous coals. For subbituminous and lignitic coals the calculated values show deviations from the determined values often as great as 4 and 5 percent. Table III summarizes such errors for various ranks of coal. Twenty to thirty representative coals were used for each rank.

TABLE III

COMPARISON OF ERRORS IN CALCULATED CALORIFIC VALUES FOR VARIOUS RANKS OF COAL

Rank of Coal	Mean Algebraic Error percent	Maximum Plus Error percent	Maximum Minus Error percent	Oxygen in Moisture-Free and Ash-Free Coal percent
Peat	-7.4	...	11.0	34.4
Lignite	-3.1	...	5.4	23.4
Subbituminous coal	-1.4	0.9	3.7	19.1
Bituminous coal, Rocky Mountain field	-0.2	1.0	1.6	10.3
Bituminous coal, Illinois field	-0.1	1.8	1.4	10.7
Bituminous coal, Appalachian field	+0.2	1.3	1.5	7.1
Low-volatile and medium-volatile bituminous coal from Pennsylvania and West Virginia	+0.7	1.6	0.5	3.1
Anthracitic coal, Pennsylvania	+0.6	1.5	0.3	3.1

The average oxygen content of each rank of coal is listed also. This table shows that the magnitude of the errors changes progressively with the oxygen content of the coals, indicating that part of the oxygen of the high-oxygen coals is associated with the carbon and not entirely with the hydrogen as assumed in Dulong's formula.

Other errors in calculated values may result from various causes. Oxygen in coal is not determined directly but is calculated by difference, and so it contains the summation of errors of analysis. In the Dulong formula the heats of combustion used for carbon and hydrogen are those of the free elements which are not the same as those of these elements as constituents of chemical compounds.

³⁶ Jarrier, P., *Chaleur et ind.*, **10**, 107-12 (1929); *Fuel*, **8**, 486-91 (1929).

³⁷ Veron, M., *Chaleur et ind.*, **10**, 433-8 (1929).

³⁸ Fieldner, A. C., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper 586*, 29-34 (1938).

Other formulas have been proposed for calculating calorific value from ultimate analyses. A number that have been introduced in recent years are summarized in Table IV. Most of them are modifications of the Dulong type of formula, the main difference being the assumptions concerning the chemical combination of the oxygen with the other elements in the coal.

Mott and Spooner have developed a formula of this type that is based on the assumption that two-thirds of the oxygen is associated with the hydrogen and one-third with the carbon of the coal.⁴⁷ Their work shows that the calorific value of carbon in bituminous coal does not vary and may be taken as $8,000 \pm 10$ calories per

gram, but that the heat of decomposition of coal should be allowed for in the formula, which is done by using 8,030 calories per gram as the calorific value of carbon in coal. The formula gives good agreement between determined and calculated values for various British and American coals ranging from anthracite to subbituminous coals that contain less than 15 percent oxygen. A modified formula was proposed for coals that contain more than 15 percent oxygen.

The Grumell and Davies formula,⁴⁴ illustrating a different type, is based on the assumption that the amount of heat evolved by fuels on complete combustion is proportional to the amount of oxygen

TABLE IV

FORMULAS FOR CALCULATION OF CALORIFIC VALUE FROM ULTIMATE ANALYSIS, DRY ASH-FREE BASIS

Author	Year Published	Formula
Strache-Lant ³⁹	1924	Cal. per g. = $81.37C + 342.2H - 36.6O + 25S$
Steuer ⁴⁰	1926	= $81(C - \frac{3}{8}O) + 57(\frac{3}{8}O) + 345(H - \frac{1}{16}O) + 25S$
Vondracek ⁴¹	1927	= $(89.1 - 0.062C)C + 270(H - \frac{1}{16}O) + 25S$
D'Huart ⁴²	1930	= $81C + 342.5H + 22.25S - 30.4O$
Schuster ⁴³	1931	= $(254 + 0.355O) \left[\frac{C}{8} + H - \frac{O - S}{8} \right]$
Grumell and Davies ⁴⁴	1933	= $(3.635H + 235.9) \left[\frac{C}{8} + H - \frac{O - S}{8} \right]$
Gumz ⁴⁵	1938	= $81.3C + 297H + 15N + 45.6S - 23.5O$
Sümeği ⁴⁶	1939	= $81 \left[C - \left(\frac{O}{2} \right) 0.75 \right] + 345 \left[H - \left(\frac{O}{2} \right) 0.125 \right] + 25S$
Mott and Spooner ⁴⁷	1940	= $80.3C + 339H - 34.7O + 22.5S$ = $80.3C + 339H - (36.6 - 0.172O)O + 22.5S$ ⁴⁸

³⁹ Strache, H., and Lant, R., *Kohlenchemie*, Akademische Verlagsgesellschaft, Leipzig, 1924, p. 476.

⁴⁰ Steuer, W., *Brennstoff-Chem.*, **7**, 344-7 (1926).

⁴¹ Vondracek, R., *ibid.*, **8**, 22-3 (1927).

⁴² D'Huart, K., *Die Wärme*, **53**, 313-7 (1930); *Chem. Abs.*, **24**, 5966 (1930).

⁴³ Schuster, F., *Glückauf*, **67**, 232-5 (1931); *Brennstoff-Chem.*, **15**, 45-6 (1934).

⁴⁴ Grumell, E. S., and Davies, I. A., *Fuel*, **12**,

199-203 (1933); *Colliery Guardian*, **146**, 1154-5 (1933).

⁴⁵ Gumz, W., *Feuerungstechnik*, **26**, 322-3 (1938); *Chem. Abs.*, **33**, 6556 (1939).

⁴⁶ Sümeği, L., *Magyar Mernők Egyesülete Közlönye*, **73**, 345-6 (1939); *Chem. Abs.*, **34**, 1459 (1940).

⁴⁷ Mott, R. A., and Spooner, C. E., *Fuel*, **19**, 226-31, 242-51 (1940).

⁴⁸ Modified formula for coals having over 15 percent oxygen.

TABLE V

FORMULAS FOR CALCULATION OF CALORIFIC VALUE FROM PROXIMATE ANALYSIS

Author	Year Published	Formula	Remarks
Goutal ⁴⁹	1902	Cal. per g. = $82C + aV$	C = percent fixed carbon V = percent volatile matter a = function of V' , or dry, ash-free V
Chizhevskii and Verkhovtzev ⁵⁰	1927	Cal. per g. = $82C + aV$	Goutal formula applied to coals containing over 40 percent volatile matter
Nakamura ⁵¹	1929	Cal. per g. = $-bF$	F = percent fixed carbon b = 78 V = percent volatile matter a = function of V
Bowlby ⁵²	1929	Btu per lb = $XVM + 145.5FC + 40.5S$	X = a constant depending on colliery
Schmit ⁵³	1925	Cal. per g. = $8,100 + 2.95X(40 - X)$	X = percent volatile matter of dry, ash-free coal
Gumz ⁵⁴	1931	Cal. per g. = $8,150 + 6,543V - 17,308V^2$ (gross) = $8,150 + 4,489V - 13,864V^2$ (net)	V = fraction of volatile matter of dry, ash-free coal
Forrester ⁵⁵	1932	Cal. per g. = $80.8C + kV$	k varies from 90.5 to 103.25 for coals examined
Chang and Hsieh ⁵⁶	1934	Cal. per g. = $81FC + (A + B \log R)VM$	A and B are functions of R
Koo and Fan ⁵⁷	1935	Cal. per g. = $82FC + aVM + b$	b is a function of $\frac{VM}{FC}$
Florentin ⁵⁸	1936	Cal. per g. = $82C + aV$	Goutal formula applied to anthracites and semicokes
Scott, Jones and Cooper ⁵⁹	1939	Btu per lb = $14,803 + 75.8V - 167.4A$	For anthracites V = percent volatile matter A = percent ash

⁴⁹ Goutal, M., *Compt. rend.*, **135**, 477-9 (1902); *J. Soc. Chem. Ind.*, **21**, 1267 (1902).

⁵⁰ Chizhevskii, N., and Verkhovtzev, M., *J. Russ. Met. Soc.*, No. 1, **1927**, 93-101; *Chem. Abs.*, **24**, 943 (1930).

⁵¹ Nakamura, K., *J. Fuel Soc. Japan*, **8**, 1323-8 (1929); *Fuel*, **9**, 54 (1930).

⁵² Bowlby, J. L., *Trans. Can. Inst. Mining Met.*, **32**, 469-90 (1929).

⁵³ Schmit, *Chaleur et ind.*, **6**, 524-5 (1925).

⁵⁴ Gumz, W., *Feuerungstech.*, **19**, 1-3 (1931); *Chem. Abs.*, **25**, 1968 (1931).

⁵⁵ Forrester, C., *Colliery Guardian*, **145**, 382-4 (1932).

⁵⁶ Chang, K., and Hsieh, M., *J. Chem. Eng. (China)*, **1**, 127-35 (1934); *Chem. Abs.*, **29**, 2690 (1935).

⁵⁷ Koo, E. C., and Fan, C., *Ind. Research (China)*, **4**, 377-83 (1935); *Chem. Abs.*, **30**, 2726 (1936).

⁵⁸ Florentin, D., *Ann. fals.*, **29**, 545-6 (1936); *Chem. Abs.*, **31**, 2776 (1937).

⁵⁹ Scott, G. S., Jones, G. W., and Cooper, H. M., *Ind. Eng. Chem.*, **31**, 1025-7 (1939).

or air consumed and that this proportional relation is not constant but varies with the hydrogen content. The Schuster formula⁴³ is similar, the proportional relation being based on the oxygen content of the coal.

Grumell and Davies applied their formula and those of Vondracek⁴¹ and Dulong to a large number of representative British coals with conclusions as follows:

(1) The Vondracek formula appears to apply equally to all fuels if agreement to within 100 calories is accepted. A possible exception may be found with very low-carbon fuels, below 80 percent carbon, but in view of the fact that fuels of this rank frequently contain large percentages of moisture and oxygen, it is possible that actual calorific values may be a shade low.

(2) The Dulong formula gives excellent agreement up to 86 percent carbon.

(3) As a method of checking the determined calorific value, the Vondracek formula is superior to the Dulong formula, its universal applicability being its principal feature.

(4) A modified formula has been developed which is universally applicable and is more accurate than the Vondracek formula.

Proximate Analysis. Various formulas for calculating calorific values from proximate analyses have been proposed, a number of which are listed in Table V. Such formulas, based on variation of calorific value with variation of volatile matter, are subject to the uncertainty of the volatile-matter determinations, and to the variable proportion of inert constituents, such as carbon dioxide and water, present in the volatile matter of the various ranks of coal. This inert material may range from 4 percent of the total volatile matter in low-volatile bituminous coal to as much as 42 percent in subbituminous coal.⁶⁰ Also, the percentage composition of the various

combustible constituents, such as hydrocarbons, hydrogen, and carbon monoxide, vary for the different ranks of coal.

Probably Goutal's formula⁴⁹ has been used most widely for calculating calorific values from proximate analysis, in which

$$\text{Calories} = 82C + aV$$

where C = percent fixed carbon.

V = percent volatile matter.

a = a figure that varies with V' , the volatile-matter content on the "dry, ash-free" or "pure-coal" basis

$$V' = \frac{100V}{C + V}$$

Goutal gave the following relationships between V' and a :

V'	5	10	15	20	25	30	35	38	40
a	145	130	117	109	103	98	94	85	80

Taylor and Patterson⁶¹ tested this formula on eighteen typical British coals and concluded that the method gives a means of calculating the calorific value of coals not excessively high in oxygen content with a degree of accuracy that closely approximates the results obtained by the bomb method. With the exception of a low-volatile coking coal and a high-volatile, high-oxygen gas coal, the calculated Btu values showed a maximum difference of 5.4 percent from those determined by the bomb-calorimeter method. The calculated results for ten of these coals were within 1.6 percent of the determined values.

CONSTANCY OF CALORIFIC VALUE OF COAL IN LIMITED AREAS

The calorific value of the pure coal substance, or the dry, mineral-matter-free coal, from a given mine and coal bed is

⁶⁰ Porter, H. C., and Ovitz, F. K., *U. S. Bur. Mines, Bull.* 1, 28 (1910).

⁶¹ Taylor, R. A. A., and Patterson, W. S., *J. Soc. Chem. Ind.*, 48, 105-8T (1929).

generally quite constant, and if this value is known the calorific value of any shipment of coal from the mine can be calculated satisfactorily, provided that the moisture, ash, and sulfur content are determined. The calorific value of the dry, mineral-matter-free coal, called unit Btu by Parr,⁶² is usually calculated by the application of empirical formulas applied to the coal analyses. Graphic⁶³ methods are used occasionally for special work. The constancy of the dry, mineral-matter-free calorific value of coals from the same source is used often by coal chemists as a check on the laboratory determinations. It has been used to calculate the heating value of various coals.⁶⁴ The large number of analyses of mine samples available in publications of the Bureau of Mines and of various state geological surveys afford a ready means of determining the unit Btu values of many coals.

A compilation of moisture- and ash-free calorific values of bituminous coals of Pennsylvania⁶⁵ shows that the deviation of the moisture- and ash-free calorific value of any individual sample from the average of a given mine is usually less than 1 percent when calculated as follows:

Btu of moisture- and ash-free coal

$$\frac{\text{Btu as determined}}{100 - (\text{Moisture} + \text{Ash})} \times 100$$

Most of these coals contained less than 12 percent ash and 2 percent sulfur. Calorific values of various shipments of such coals can be calculated within an accuracy

⁶² Parr, S. W., and Wheeler, W. F., *Univ. Illinois Eng. Exp. Sta., Bull.* **37** (1909), 67 pp.

⁶³ Stansfield, E., and Sutherland, J. W., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 614-26 (1930).

⁶⁴ Lategan, P. N., *Fuel*, **6**, 447-8 (1927).
King, K. Y., and Hsia, W. S., *Singuan Fuel Lab. Geol. Survey China, Contrib.* **19** (in English), October, 1936.

⁶⁵ Fieldner, A. C., *Ind. Eng. Chem.*, **5**, 270-82

of 1 percent by multiplying the average moisture- and ash-free calorific value by $[100 - (\text{Moisture} + \text{Ash})] \div 100$, where the moisture and ash are percentages of the individual samples representing the shipments. With coals having more than 2 percent sulfur, a further correction should be applied.

The ash obtained on analysis of a coal sample usually weighs less than the mineral matter from which it is derived because of loss during ashing of combined water of some of the ash-forming minerals, and the conversion of pyrite (FeS_2) to ferric oxide (Fe_2O_3). A formula that takes these items into consideration and that is more accurate than the simple moisture- and ash-free formula is as follows:

Btu of moisture- and mineral-matter-free coal

$$\frac{\text{Btu as determined}}{\left\{ \frac{100 - (\text{Moisture} + 1.1)}{\text{ash} + 0.1 \text{ sulfur}} \right\}} \times 100$$

The sulfur correction of 0.1 is empirical and may be eliminated for coals having less than 2 percent sulfur. The apparent ratio of mineral matter to ash is assumed to be equal to 1.1. This formula has been used extensively in preference to the moisture- and ash-free formula; it is one of the two optional formulas recommended in the *Standard Specifications for Classification of Coals by Rank* of the American Society for Testing Materials.⁶⁶ If the Btu of the moisture- and mineral-matter-free coal from a given mine and bed is known, the Btu of various shipments of coal from this mine can be calculated quite accurately by this formula, after the moisture, ash, and sulfur content are determined.

Another formula that gives still more accurate results and that has been found to be generally applicable to all coals within

⁶⁶ *ASTM Standards*, Pt. III, 1939, pp. 1-6.

the limits of such empirical formulas is that developed by Parr,⁶⁷ as follows:

Btu of moisture- and mineral-matter-free coal

$$\frac{\text{Btu as determined} - 50 \text{ sulfur}}{\left\{ \frac{100 - (\text{Moisture} + 1.08)}{\text{ash} + 0.55 \text{ sulfur}} \right\}} \times 100$$

In this formula the mineral matter or noncoal substance is considered to be as follows:

$$\text{Noncoal} = M + A + \frac{5}{8}S + 0.08(A - \frac{1}{8}S)$$

where M = moisture.

A = ash.

S = sulfur.

$\frac{5}{8}S$ restores the Fe_2O_3 as weighed in the ash to FeS_2 , as weighed in the coal, 3 oxygens or 48 in the ash having been originally 4 sulfurs or 128 in the coal.

$\frac{1}{8}S$ represents the equivalent of Fe_2O_3 as weighed in the ash; that is, the Fe_2O_3 molecule, 160, is $\frac{1}{8}$ of the sulfur present in the coal.

$(A - \frac{1}{8}S)$ is the ash as weighed minus the Fe_2O_3 , and 0.08 is a constant applied to the iron-free ash to restore the water of hydration to the earthy matter less iron pyrite, thus representing the true amount of shaly constituent as weighed in the original coal.

Simplifying, the equation becomes

$$\text{Noncoal} = 1.08A + \frac{21}{40}S$$

In use, Parr changed the fraction $\frac{21}{40}$ to $\frac{22}{40}S$ or $0.55S$ to simplify the calculation and possibly promote accuracy by partly compensating for the sulfur, which may not be present in the pyritic form.

The formula for mineral-matter-free coal is then: Mineral-matter-free coal = $100 - (\text{Moisture} + 1.08 \text{ ash} + 0.55 \text{ sulfur})$.

The factor $50S$ is an approximate correc-

tion applied to the Btu as determined to correct for the heat of combustion of the sulfur in the coal.

In 1909, Parr⁶² published his investigations on Illinois coals to devise suitable formulas for calculating calorific values of moisture-free and mineral-matter-free coal. Since that time other investigators⁶⁸ have conducted similar studies, and apparently Parr's original formula is as good as any simple formula that can be devised for general application to various coals.

CALORIFIC VALUE AS A BASIS FOR COAL CLASSIFICATION

In 1928 Parr⁶⁷ published a scheme for classifying coals of the United States, in which unit Btu or the calorific values of dry, mineral-matter-free coal were used in conjunction with volatile matter to divide coals into various groups according to their degree of metamorphism.

In 1927 the Sectional Committee on Classification of Coals was organized by the American Society for Testing Materials under the rules of the American Standards Association. To this committee was assigned the development of a classification for coals of North America, ranging from lignite to anthracite, the classification to be based on such chemical and physical characteristics as would make the plan most readily adaptable to industrial and commercial use on a national scale. The Associate Committee on Coal Classification

⁶² Fieldner, A. C., and Selvig, W. A., *Trans. Am. Inst. Min. Met. Engrs.*, **88**, 597-611 (1930).
⁶³ Fish, F. H., and Addlestone, J. A., *Ind. Eng. Chem., Anal. Ed.*, **3**, 155-8 (1931).
⁶⁴ Fieldner, A. C., Selvig, W. A., and Gibson, F. H., *Trans. Am. Inst. Min. Met. Engrs.*, **101**, 224-35 (1932).
⁶⁵ Nicolls, J. H. H., and Swartzman, E., *Canada Dept. Mines, Mines Branch, Investigations of Fuels and Fuel Testing*, 1932, No. 737, 1934, pp. 63-75.
⁶⁶ Hertzog, E. S., *Fuel*, **12**, 112-7 (1933).
⁶⁷ Thiessen, G., Cady, G. H., Rees, O. W., and Reed, F. H., *Illinois Geol. Survey, Rept. Investigations* **32** (1934), 99 pp.

⁶⁷ Parr, S. W., *Univ. Illinois Eng. Exp. Sta., Bull.* **180** (1928), 59 pp.

and Analysis of the National Research Council of Canada cooperated actively with the Sectional Committee.

After extensive studies of various systems of coal classification and their application to coals of North America, the committee in 1934 recommended a system for classification of coals by rank,⁶⁹ that is, according to their degree of metamorphism or progressive alteration in the natural series from lignite to anthracite. This classification was adopted in amended form as standard in 1937 and revised in 1938.⁶⁶

Calorific values play an important role in this system of classification as the basic scheme of classification is according to fixed carbon and calorific value expressed in Btu on the mineral-matter-free basis. The higher-rank coals are classified accord-

ing to fixed carbon on the dry basis; the lower-rank coals, according to calorific values expressed in Btu on the moist basis, that is, with the coal containing its natural bed moisture but not including any visible water on the surface of the coal.

Coals having calorific values less than 14,000 Btu on the moist, mineral-matter-free basis are classified according to Btu provided that the fixed carbon on the dry, mineral-matter-free basis is less than 69 percent. The application of this system of classification to coals of the United States and Canada has proved very useful,^{70, 71} and the system is practical by reason of its simplicity. (See Chapter 2.)

⁷⁰ Fieldner, A. C., Selvig, W. A., and Frederic, W. H., *U. S. Bur. Mines, Rept. Investigations* **3296R** (1939), 22 pp.

⁷¹ *Nat. Research Council Can. Publ.* **S14** (1939), 26 pp.

⁶⁶ *Proc. ASTM*, **34**, Pt. I, 834-40 (1934).

CHAPTER 5

HARDNESS, STRENGTH, AND GRINDABILITY OF COAL *

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HARDNESS

Considerable information is available on the properties of coal that are related to its hardness, namely, its friability and grindability, but little is known of the hardness of coal as an intrinsic property. This circumstance is attributable to the limited commercial significance of the hardness of coal compared with the economic importance of the properties of friability and grindability.

The scratch hardness of a series of coals was determined by Heywood¹ by measuring the load on a pyramidal steel point required to make a scratch 100 microns in width on the polished surface of a specimen. Shales, calcite, and pyrite were tested for comparison, a diamond point being used for the last two materials (see Table I).

The scratch hardness of anthracite is about 6 times that of the softest coal tested, whereas pyrite is nearly 20 times as hard. Relative results of the same magnitude

* Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

¹ Heywood, H., *J. Inst. Fuel*, **9**, 94-105 (1935); *Colliery Guardian*, **151**, 898-900, 941-4 (1935).

TABLE I

RESULTS OF SCRATCH HARDNESS TESTS,
ACCORDING TO HEYWOOD¹

Material	Scratch Hardness Relative to Barnsley Soft Coal
Anthracite, Great Mountain	1.70
Anthracite, Red Vein	1.75
Welsh steam	0.29
Barnsley hards	0.85
Barnsley softs	1.00
Illinois coal	1.10
Cannel	0.92
Carbonaceous shale	0.69
Shale	0.32
Pyrite	5.71
Calcite	1.92

were found for anthracite and cannel coal by O'Neill,² who made indentation hardness tests of a few British coals. A singular feature of O'Neill's work was the fact that durain, the reputedly hard component of coal, was found to be only slightly harder than vitrain and cannel coal. In contrast, Matthes³ found the hardness of durain (Mattkohle) to be 68 percent compared with only 17 percent for vitrain (Glanzkohle), 7 percent for clay bands,

² O'Neill, H., *J. Inst. Fuel*, **10**, 351 (1937).

³ Matthes, T., *Glückauf*, **70**, 757-64 (1934).

and 80 percent for pyrite bands. The hardness figures of Matthes represent the percentage of rebound obtained when the specimen is struck by a small ball-peen hammer swinging as a pendulum. His apparatus, called a duroscope, is portable and is suitable for testing coal in place in the mine.

For comparison, Heywood tested the series of materials used in his scratch hardness tests to determine their resistance to the abrasive action of emery cloth. These two methods of testing placed the more brittle materials in the same relative order of hardness, but carbonaceous shale and cannel coal, although comparatively soft, showed a high resistance to abrasion owing to their toughness. The resistance of coals to abrasion, characterized as specific strength, was studied also by Šimek, Pulkrábek, and Coufalík,⁴ who utilized the abrasive action of a blast of sharp-edged steel powder impinging on the surface of a specimen; however, comparative results for different coals or coal components were not given.

Although the resistance of coals to abrasion may have no commercial significance, its counterpart, the abrasiveness of coal, is a factor of considerable economic importance. Hardgrove⁵ has shown that the wear of grinding elements due to the abrasive action of coal results in maintenance charges that constitute one of the major items in the cost of grinding coal for use as pulverized fuel. Moreover, as coals vary widely in abrasiveness, this factor must be considered when coals are selected for pulverized-fuel plants. A standardized, simple laboratory method of evaluating the abrasiveness of coal would, like the stand-

ard grindability tests now available, assist in the selection of coals suitable for use in pulverized form. Work directed toward this end is being conducted by the U. S. Bureau of Mines, but results are not yet available.

Actually, the abrasiveness of coal may be determined more by the nature of its associated impurities than by the nature of the coal substance. Heywood's work showed pyrite to be 20 times harder than coal, and the individual grains of sandstone, another common impurity in coal, also are hard and abrasive.

STRENGTH

Interest in the compressive strength of coal arises largely from its relationship to the strength of coal pillars used for roof support in mining operations. As early as 1900 the Engineers' Club of Scranton, Pa., sponsored tests of the crushing strength of anthracite from the northern anthracite field of Pennsylvania.⁶ The 423 samples tested were in the form of prisms having bases 2 inches square, cut parallel to the bedding planes of the coal, and having heights of 1, 2, and 4 inches. Compression was applied perpendicular to the bedding planes. The crushing strengths of the prisms 1 inch high ranged from 3,200 to 10,892 pounds per square inch and averaged about 6,000 pounds per square inch. Testing prisms of three heights demonstrated that the compressive strength of coal is inversely proportional to the square root of the height of the specimen tested.

In a subsequent investigation Daniels and Moore⁷ showed that the strength of a bituminous-coal specimen is influenced also by its lateral dimensions, the smaller speci-

⁴ Šimek, B., Pulkrábek, J., and Coufalík, F., *Mitt. Kohlenforsch. Inst. Prag*, **2**, 173-93 (1935).

⁵ Hardgrove, R. M., *Seventeenth Fuel Eng. Meeting, Fuel Eng. Div., Appalachian Coals Inc., Proc.*, **3**, 311-28 (1937).

⁶ Griffith, W., and Conner, E. T., *U. S. Bur. Mines, Bull.* **25**, 77-82 (1912).

⁷ Daniels, J., and Moore, L. D., *Eng. Mining J.*, **84**, 263-8 (1907).

mens showing greater strength than the larger. This relationship between compressive strength and size of test specimen is shown clearly by the results obtained by Rice and Enzian⁸ given in Table II.

TABLE II

MAXIMUM COMPRESSIVE STRENGTH OF COAL BLOCKS FROM PITTSBURGH SEAM, ACCORDING TO RICE AND ENZIAN⁸

Number of Specimens Tested	Range in Size	Average Maximum Load, pounds per square inch
6	2.5- to 4-inch cubes	2,486
3	7- to 8-inch cubes	2,170
3	10- to 12-inch cubes	2,008
1	12 by 12 by 18 inches high	1,152
1	Roughly 30-inch cube	817
1	Roughly 54-inch cube	306

The lesser strength of the larger blocks of coal is attributed to the presence of fracture planes or cleats which weaken the specimen. The smaller test pieces, being free of fractures, reveal the strength of the coal substance. A factor that probably contributes to the lower strength of large blocks of coal tested in the laboratory is the difficulty of mining large blocks and transporting them from the mine to the laboratory without imposing strains that start disintegration along the cleats. To avoid this source of error Greenwald, Howarth, and Hartmann⁹ devised a method of testing pillars of coal in place in the mine. When tested in place, Pittsburgh-bed coal shows somewhat greater compressive strength than the largest cubes of Table II.

Lawall and Holland¹⁰ determined the compressive strength and secant modulus

⁸ Rice, G. S., and Enzian, C., *U. S. Bur. of Mines, Bull.* **303** (1929), 44 pp.

⁹ Greenwald, H. P., Howarth, H. C., and Hartmann, I., *U. S. Bur. Mines, Tech. Paper* **605** (1940), 22 pp.

¹⁰ Lawall, C. E., and Holland, C. T., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 100-13 (1932).

of elasticity of coals from 11 beds in West Virginia. Three-inch cubes were tested with the loads applied parallel as well as perpendicular to the bedding planes. With the stress applied perpendicular to bedding, the strength of the coals ranged from an average of 1,682 pounds per square inch for 9 samples from the Upper Freeport Seam to an average of 4,893 pounds per square inch for 10 samples from the No. 5 Block Seam. The corresponding secant moduli of elasticity ranged from 373,000 to 615,000. Stresses applied parallel to the bedding planes gave ultimate strengths ranging from 68 to 95 percent of those for perpendicular loads. Loads applied in either direction produced a permanent deformation or set if the stress was relieved before the crushing strength was reached, but the permanent deformation was much greater for loads applied parallel to the bedding planes.

Czechoslovak anthracites tested by Pulkrábek¹¹ also showed greater strength under compression applied perpendicular to the bedding planes; but, in contrast, lignites appeared to be about equally strong in both directions. In tests of English coals, Heywood¹ found that badly fissured coals, even when tested as 1-inch cubes, may have greater strength parallel to the bedding planes than perpendicular to them. For example, Welsh steam coal was more than twice as strong in parallel compression.

Bode¹² noted a relationship between the compressive strength of coals and their petrographic composition. Coals containing more than 12 percent vitrain had strengths of 23 to 90 kilograms per square centimeter (330 to 1,280 pounds per square inch) and were characterized by

¹¹ Pulkrábek, J., *Mitt. Kohlenforsch. Inst. Prag*, **3**, 147-54 (1937).

¹² Bode, H., *Glückauf*, **69**, 296-7 (1933).

gradual failure of the test specimen. Coals containing less than 12 percent vitrain had strengths of 163 to 346 kilograms per square centimeter (2,320 to 4,920 pounds per square inch) and failed explosively.

FRIABILITY

One measure of the strength of coal is its ability to withstand degradation in size on handling. The tendency toward breakage on handling, friability, depends on toughness, elasticity, and fracture characteristics as well as on strength, but despite this fact the friability test is the measure of coal strength used most frequently. Friability is of interest primarily because friable coals yield smaller proportions of the coarse sizes which still command a premium in price on the ordinary market, despite the increasing demand for the finer sizes. Another important economic aspect of friability is the increased amount of surface produced in handling friable coals. This surface allows more rapid oxidation; hence conditions are more favorable for spontaneous ignition, loss in coking quality in coking coals, and other changes that accompany oxidation. These economic aspects of the friability of coal have provided the incentive toward development of laboratory friability tests.

The tumbler test for measuring coal friability was developed by Nicolls¹³ in 1926, modified as to the method of expressing results by Yancey, Johnson, and Selvig,¹⁴ and later adopted in simplified form as a tentative standard method of the American Society for Testing Materials.¹⁵ This test employs a cylindrical

porcelain jar mill, 7.25 by 7.25 inches in size and fitted with three lifters that assist in tumbling the coal. A 1,000-gram sample of coal sized between 1.5- and 1.05-inch square-hole screens is tumbled in the mill (without grinding medium) for 1 hour at 40 rpm. The coal is then removed and screened on square-hole sieves with openings of 1.05, 0.742, 0.525, 0.371, 0.0469, and 0.0117 inch. Friability is reported as the percentage of reduction in average particle size during the test; for example, if the average particle size of the tumbled coal was 75 percent of that of the original sample, the friability would be 25 percent.

In 1929, Smith¹⁶ described a drop shatter test for determining the friability of coal, which was similar to the standard method for the shatter test of coke¹⁷ of the American Society for Testing Materials; later, Smith's method, with some modifications, was adopted as a tentative standard of the American Society for Testing Materials.¹⁸ In the standard method a 50-pound sample of coal sized between 3- and 2-inch round-hole screens is dropped twice from a drop-bottom box onto a steel plate 6 feet below the box. The material shattered by the two drops is then screened over round-hole screens with 3-, 2-, 1.5-, 1-, 0.75-, and 0.5-inch openings and its average particle size calculated. The average size of the material, expressed as a percentage of the size of the original sample, is termed the "size stability," and its complement, the percentage of reduction in average particle size, is termed the "percentage friability." Provision is made for testing sizes other than that stipulated for the standard test to permit comparison of different sizes of the same coal.

¹³ Nicolls, J. H. H., *Can. Dept. Mines, Mines Branch, Invest. Fuels Testing, Bull. 644* (1926), 20-35 pp.

¹⁴ Yancey, H. F., Johnson, K. A., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper 512* (1932), 94 pp.

¹⁵ *Am. Soc. Testing Materials, Standards, 1939*, Pt. III, 576-9.

¹⁶ Smith, C. M., *Illinois Eng. Exp. Sta., Bull. 196* (1929), 47 pp.

¹⁷ *Am. Soc. Testing Materials, Standards, 1939*, Pt. III, 70-2.

¹⁸ *Ibid.*, pp. 570-5.

Vogel and Quass¹⁹ utilized the shatter test in a study of the friability of South African coals and found that the products of the shatter test conformed to the Rosin and Rammler equation of size distribution.²⁰ They suggested, therefore, that the constants of the equation be used in place of calculated friability values to represent friability characteristics. A more recent similar investigation²¹ has shown that, although the Rosin and Rammler law describes accurately the size composition of the products obtained in shatter tests of the softer coals, it cannot be applied satisfactorily to coals that are highly resistant to breakage.

Pulkrábek²² developed a shatter test in which 20 pieces of coal greater than 20 millimeters in size are dropped 150 times from a height of 1 meter. The shatter index is taken as the weight of material smaller than 10 millimeters in size after the test.

A comparison of shatter and tumbler methods for measuring the friability of coal made by Yancey and Zane²³ showed that a coal which is susceptible to degradation in size by shattering on impact is not necessarily as susceptible to breakage by abrasion or attrition. A coal may have these two properties in different degrees. The shatter test appears best suited to measurement of the breakage that occurs in handling the larger sizes of coal in thin layers, but it does not measure so well the breakage that occurs when coal is handled

in mass. The tumbler test, utilizing both shatter and attrition forces, is probably better suited to ordinary use. Gilmore and Nicolls²⁴ also have compared the two types of friability tests and have concluded that both are necessary to define completely the strength and breaking properties of coals. These investigators felt that the tumbler test is more suitable for estimating the behavior of coals under severe conditions of handling and that the shatter test is more suitable for estimating how coals will withstand more gentle treatment.

The advent of laboratory friability tests has made possible a correlation between the friability of coal and its rank. A summary of the results of 235 friability determinations on coals of various ranks from Washington and from one or more important seams in Pennsylvania, West Virginia, Maryland, Kentucky, Illinois, North Dakota, Montana, and Wyoming, by Yancey, Johnson, and Selvig,¹⁴ is given in Table III.

TABLE III

AVERAGE FRIABILITY VALUES OF DIFFERENT RANKS OF COAL, ACCORDING TO YANCEY, JOHNSON, AND SELVIG¹⁴

Rank of Coal	Number of Tests	Friability * percent
Anthracite	36	33
Semibituminous	27	70
Bituminous	87	43
Subbituminous A	40	30
Subbituminous B	29	20
Lignite	16	12

* Results obtained before the American Society for Testing Materials tumbler procedure was developed; 3 hours of tumbling instead of present standard 1-hour period.

²⁴ Gilmore, R. E., and Nicolls, J. H. H., *Proc. Am. Soc. Testing Materials*, 1937, Pt. II, 421-35. Gilmore, R. E., Nicolls, J. H. H., and Connell, G. P., *Can. Dept. Mines, Mines Branch, Bull.* 762 (1935), 102 pp.

¹⁹ Vogel, J. C., and Quass, F. W., *J. Chem. Met. Min. Soc. S. Africa*, 37, 469-78, 553-6 (1937).

²⁰ Rosin, P., and Rammler, E., *J. Inst. Fuel*, 7, 29-36 (1933). Bennett, J. G., *ibid.*, 10, 22-39 (1936).

²¹ Geer, M. R., and Yancey, H. F., *Trans. Am. Inst. Mining Met. Engrs.*, 130, 250-69 (1938).

²² Pulkrábek, J., *Mitt. Kohlenforsch. Inst. Prag*, 3, 155-77 (1937).

²³ Yancey, H. F., and Zane, R. E., *U. S. Bur. Mines, Rept. Investigations* 3215 (1933), 24 pp.

Lignites were found to be the least friable of all coals, and friability increased with an increase in coal rank to a maximum for coals of the semibituminous (low-volatile) group. The friability of anthracites is comparable to that of subbituminous coals; both are stronger than bituminous coals and decidedly more resistant to breakage than the very friable semibituminous coals.

In their study of West Virginia coals, Lawall and Holland¹⁰ found that friability could be correlated with fuel ratio and thus used to indicate the boundary between the high- and low-volatile coals of that state.

Although a relationship does exist between friability and rank it can be described in general terms only, as coals of the same rank vary widely in friability. Hertzog and Cudworth²⁵ have shown that the high-volatile A bituminous coals of Alabama range in friability from a low of 17 percent to a high of 60 percent. A similar range in the friability of Canadian coals of the same rank was found by Gilmore and Nicolls.²⁶

The relationship between the friability of coal and its rank has a bearing on its tendency to heat or fire spontaneously. As shown by Stopes and Wheeler,²⁷ and more recently by Schmidt and Elder,²⁸ the friable, low-volatile coals, because of their high rank, do not oxidize readily despite the excessive fines and attendant increased surface they produce on handling. Coals of somewhat lower rank, which oxidize more readily, usually are relatively non-

friable, hence they resist degradation in size with its accompanying increase in the amount of surface exposed to oxidation. In oxidation and friability tests of eight commercially important coals Schmidt and Elder found that if the coals were arranged in the order of decreasing friability the order was identical with that of increasing characteristic rate of oxidation. Thus the tendency of coals toward self-heating is counteracted to some extent by the relative resistance to breakage of the more troublesome lower-rank coals. With coals of subbituminous rank, disintegration by slacking supplements that due to breakage on handling.

The work of Hoffmann and Kühlwein²⁹ with Saar, Ruhr, Upper Silesia, and English coals, as well as that of McCabe³⁰ with Illinois coals, has demonstrated that the banded petrographic constituents of coal—vitrain, clarain, durain, and fusain—differ materially in strength and hence in friability and grindability. Fusain is structurally the weakest of the components; vitrain is brittle but stronger than fusain; and clarain is relatively strong and nonfriable. Durain, when present, is the strongest of the group. Kühlwein and Abramski³¹ have reported that the compressive strength of durain is 900 kilograms per square centimeter (12,800 pounds per square inch) compared with only 50 kilograms per square centimeter (710 pounds per square inch) for vitrain. When coal is broken in mining and preparation, this variation in strength and friability results in some segregation of the various constituents in the various sizes of

²⁵ Hertzog, E. S., and Cudworth, J. R., *U. S. Bur. Mines, Rept. Investigations* 3384 (1938), 8 pp.

²⁶ Gilmore, R. E., and Nicolls, J. H. H., *Can. Dept. Mines and Resources, Bur. Mines, Mem. Ser.*, No. 70, 1939, 25 pp.

²⁷ Stopes, M. C., and Wheeler, R. V., *Fuel*, 2, 36-7 (1923).

²⁸ Schmidt, L. D., and Elder, J. L., *Ind. Eng. Chem.*, 32, 249-56 (1940).

²⁹ Hoffmann, H., and Kühlwein, F. L., *Glückauf*, 71, 677-86, 710-3 (1935). Kühlwein, F. L., *Trans. Inst. Mining Engrs.*, 81, 358-67 (1930-1).

³⁰ McCabe, L. C., *Mining Congr. J.*, 23, No. 12, 18-9 (1937); *Mech. Eng.*, 60, 217-21 (1937).

³¹ Kühlwein, F. L., and Abramski, C., *Glückauf*, 75, 865-74, 881-90 (1939).

prepared coal. Frequently clarain and durain are concentrated in the coarser sizes, and vitrain and fusain predominate in the finer coal. Wormann³² has pointed out, however, that if durain is present in the coal bed in only thin strata it may concentrate in the finer sizes of coal despite its greater strength and resistance to breakage. These investigators agree that, as the constituents differ in composition and chemical properties, their segregation according to relative friability imparts different properties to the various commercial sizes of coal. The ash content, ash-fusing temperature, volatile-matter content, and coking properties of the constituents differ; hence, if segregation is pronounced, these properties differ in the various sizes of the same coal and cause these sizes to behave differently in coking and in combustion. Blending coals and mixing different sizes of the same coal to obtain the desired petrographic composition may become important elements of coal preparation.

GRINDABILITY

The grindability of coal, or the ease with which it may be ground fine enough for use as pulverized fuel, is a composite physical property embracing other specific properties such as hardness, strength, tenacity, and fracture. The laboratory grindability test is a valuable tool for estimating the capacity of new pulverizing equipment, for plant control, and for comparing the performance of pulverizers on different coals. Without some knowledge of how various coals behave in the grinding operation—that is, how their use affects pulverizer capacity and power requirements—coals cannot be chosen for pulverized-fuel plants that will always carry the required load if

pulverizer capacity is limited. Thus, the makers and users of pulverizing equipment, coal producers, and coal-marketing agencies have felt the need for information on the grindability of coal. Such wide interest naturally stimulated research, and a number of laboratories in the United States, Canada, England, and Germany undertook to study grindability. The work has been directed largely toward the development of methods for estimating grindability and, to a smaller extent, toward correlation of grindability with rank of coal and with pulverizer performance.

METHODS OF ESTIMATING GRINDABILITY

The fact that the energy necessary for grinding is related to the new surface produced in the operation has long been recognized. As early as 1867 Rittinger formulated his classical law of crushing which states that the energy necessary for reduction in particle size is in direct proportion to the increase in surface. It is only natural, therefore, that most grindability tests have taken the form of equating the energy expended in grinding with the new surface produced.

The voluminous literature available on the energy-surface relationship in grinding materials other than coal cannot be reviewed here; however, the recent investigations of Gross and Zimmerley³³ and Dean³⁴ warrant brief mention, as they provide general conclusions applicable to the study of coal grindability. In both investigations crushing was done in a frictionless, drop-weight machine with which

³³ Gross, J., and Zimmerley, S. R., *Trans. Am. Inst. Mining Met. Engrs.*, **87**, 7-48 (1930). Gross, J., *U. S. Bur. Mines, Bull.* **402** (1938), 148 pp.

³⁴ Dean, R. S., *Am. Inst. Mining Met. Engrs., Tech. Pub.* **660** (1936), 5 pp. Gottschalk, V. H., *U. S. Bur. Mines, Rept. Investigations* **326S**, 83-90 (1935).

³² Wormann, A., *Glückauf*, **71**, 677-86, 710-8 (1935).

the energy expended in crushing could be determined accurately. Gross and Zimmerley chose quartz for crushing, as the surface of the crushed product could be determined accurately from its rate of dissolution in hydrofluoric acid. Dean chose magnetite for a similar reason; its surface could be determined from its coercive force. Rittinger's law was found to be valid for both materials; that is, the new surface produced in each was directly proportional to the energy expended in crushing.

Investigations of the grindability of coal have been hampered by the fact that its surface can be measured only with screens or with screens in combination with elutriation, sedimentation, or microscopic counting for the finer sizes. In coal approaching pulverized-fuel size, most of the surface is present in the sizes below the lower limit of screening, and screen analyses of such material provide only a crude estimate of the surface present. The processes of elutriation, sedimentation, and microscopic counting are difficult and laborious to carry out and generally do not give sufficiently accurate results.

The Lea-Nurse,³⁵ or air-permeability, method of estimating the surface of subsieve materials has been used in grindability tests of coal by Romer.³⁶ Although this method is easily applied and rapid, its accuracy with coal has not yet been demonstrated.

Heywood¹ is one of the few investigators who has evaluated in absolute rather than purely relative terms the energy re-

quired for the production of new surface in the grinding of coals. Heywood utilized simple grinding methods, such as compression to failure in a testing machine and the impact of a falling weight, to permit accurate measurement of the net work done in crushing. As the coals were only coarsely crushed by these devices, the surface formed could be determined accurately by screening. His values for the foot-pounds of energy required to produce 1 square foot of new surface in various coals are shown in Table IV. The energy required for crushing various coals by compression was found to range from 0.86 to 10.80 foot-pounds per square foot of new surface produced.

Other investigators³⁷ who have employed crushing devices designed to measure the net energy have reported widely divergent results. Carey and Bosanquet, for example, found that 0.13 horsepower-hour per ton was required to crush coal from $\frac{1}{2}$ inch to 200-mesh size by impact or compression crushing. In contrast, Coe, Delano, and Coghill reported values ranging from 6.6 to 9.5 horsepower-hours per ton for grinding three coals from $\frac{3}{4}$ inch to 48-mesh top size. These investigators employed a specially designed, continuously operating pulverizer which simulates industrial pulverizer operation in that a balanced circulating load of material is built up in the machine.

Gunder³⁸ also has described an apparatus suitable for measuring the actual work done in grinding. This machine, known as the Brabender hardness tester, consists of a "coffee-mill" type crusher, the rotating

³⁵ Lea, F. M., and Nurse, R. W., *J. Soc. Chem. Ind.*, **58**, 277-83 (1939). Carman, P. C., *ibid.*, **57**, 225-34 (1938), **58**, 1-7 (1939). Gooden, E. L., and Smith, C. M., *Ind. Eng. Chem., Anal. Ed.*, **12**, 479-82 (1940).

³⁶ Romer, J. B., presented at the 44th annual meeting Am. Soc. Testing Materials, Chicago, Ill., June, 1941.

³⁷ Carey, W. F., and Bosanquet, C. H., *J. Soc. Glass Tech.*, **17**, 384-410 (1933). Carey, W. F., *Trans. Inst. Chem. Engrs.*, **12**, 179-83 (1934). Coe, G. D., Delano, P. H., and Coghill, W. H., *Trans. Am. Inst. Mining Met. Engrs.*, **140**, 231-41 (1942).

³⁸ Gunder, W., *Glückauf*, **74**, 641-6 (1938).

TABLE IV

RESISTANCE TO CRUSHING, MEASURED IN TERMS OF FOOT-POUNDS OF ENERGY REQUIRED TO PRODUCE 1 SQUARE FOOT OF NEW SURFACE, ACCORDING TO HEYWOOD ¹

	Attrition Test	Compression Test,		Impact † Test	Crushing-Rolls Test
		Average *	Perpendicular only		
	foot-pounds	foot-pounds	foot-pounds	foot-pounds	foot-pounds
Anthracite, Great Mountain	245	10.80	8.70	8.7	8.0
Anthracite, Red Vein	79	1.36	6.2
Welsh steam	34	0.86	1.7
Barnsley hards	51	4.01	6.42	8.0
Barnsley softs	46	3.68	5.40	6.0	7.35
Illinois coal	40	2.04	3.62	6.35
Cannel	116	7.22	11.62	13.7	9.7
Carbonaceous shale	...	11.60	15.40	..	18.5
Shale	103	2.40	3.25	23.8	15.0
Pyrite	81

* Averaged by doubling the value for compression parallel to the bedding planes, adding the value of perpendicular compression, and dividing by 3.

† Perpendicular to bedding only.

grinding element of which is driven by an electro-dynamometer. The torque of the dynamometer housing provides a measure of the resistance offered by the sample to the rotation of the grinding element. The torque is recorded automatically. No data are available on the energy required to produce unit new surface in this machine.

Heywood's data provide information that is useful in assessing the efficiency of commercial pulverizers and in showing how the efficiency of grinding is related both to the kind of force producing comminution and to the nature of the material being crushed; however, methods that involve actual measurement of energy and surface have held, in the past, little promise for ordinary use. Both the work done in

grinding and the surface of pulverized materials have been difficult to evaluate, and only with such materials as quartz and magnetite, which have measurable properties directly related to surface, has it been possible to determine the surface of subsieve material with acceptable accuracy. Moreover, grindability values expressed in absolute units of surface and energy cannot be applied directly to a coal pulverizer; they must first be converted into purely relative units.

These considerations have led most investigators to develop test methods that are based upon the relationship between energy and surface but do not require direct measurement of those quantities. Instead, the energy expended in grinding is taken as the number of revolutions of a

mill, and the new surface is approximated from the screen analysis of the ground product. Such methods yield relative grindability values.

Most methods of estimating relative grindability utilize the ordinary laboratory porcelain jar mill. The Cross³⁹ and F.R.L.⁴⁰ methods, as well as the tests developed by Schultes and Goecke⁴¹ and Pulkrábek and Coufalík,⁴² employ grinding in this type of mill. In the Cross method each coal is ground for 400 revolutions, and the amount of new surface is estimated from screen analyses of the feed and of the ground product. Coals are then rated in grindability by comparing the amount of new surface found in the test with that obtained for a standard coal. A similar procedure was followed by Pulkrábek and Coufalík.

In the F.R.L. method, coal is ground for 1,000 revolutions with a charge of sillimanite balls. The minus 100-mesh product is then screened out, and the oversize, with enough of the feed sample to replace the undersize, is reground for an additional cycle of 1,000 revolutions. This procedure is repeated for a third grinding cycle of the same length, and the weight of coal, in grams, passing the 100-mesh screen is considered as the grindability index. Schultes and Goecke also used the amount of material passing an index sieve as a measure of grindability. As an alternative, Goecke⁴³ plotted the screen analysis of the ground product and attempted to evaluate grindability by the constants of

the Rosin and Rammler equation²⁰ for size distribution.

In place of a mill, the C.I.T. roll test⁴⁴ employs a flat steel plate on which a small sample of closely sized coal is crushed by the action of a heavy steel cylinder rolled over it by hand. The new surface is estimated from the screen analysis of the ground product.

The Hardgrove test⁴⁵ utilizes a special grindability mill of the ring-and-ball type, in which a 50-gram sample of closely sized coal is ground for 60 revolutions. Originally the ground product was screened on a series of sieves to determine approximately the amount of new surface produced, and a grindability index was calculated by expressing the new surface as a percentage of that found for a standard coal. In its present form the test has been modified to require sieving the ground coal on only the 200-mesh sieve. The grindability index is calculated from the amount of undersize produced, using a corrective formula to make the results correspond closely with those obtained with the older form of surface calculations.

These methods are of the constant-work type: that is, a fixed amount of work is expended on each coal, and a grindability value is determined from the size composition of the ground material. The ball-mill⁴⁶ method is based upon a different fundamental principle, namely, that of grinding all coals to the same fineness—about that actually required for pulverized fuel—and using the relative amounts of energy required for this reduction in size as a measure of grindability. In this

³⁹ Cross, B. J., unpublished report of Subcommittee 7, Committee D5, Am. Soc. Testing Materials.

⁴⁰ Baltzer, C. E., and Hudson, H. P., *Can. Dept. Mines, Mines Branch Report*, 1933, 737.

⁴¹ Schultes, W., and Goecke, E., *Arch. Wärme-wirt.*, **13**, 253-7 (1932).

⁴² Pulkrábek, J., and Coufalík, F., *Mitt. Kohlen-forsch. Inst. Prag*, **3**, 178-92 (1937).

⁴³ Goecke, E., *Glückauf*, **70**, 435-8 (1934).

⁴⁴ Sloman, H. J., and Barnhart, A. C., *Trans. Am. Soc. Mech. Engrs.*, **56**, 773-9 (1934).

⁴⁵ Hardgrove, R. M., *Trans. Am. Soc. Mech. Engrs., Fuels Steam Power*, **54**, 37-46 (1932).

⁴⁶ Yancey, H. F., Furse, O. L., and Blackburn, R. A., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 267-94 (1934).

method, 500 grams of coal are ground in an 8-inch steel ball mill rotated by a suitable mill carrier. The relative amounts of energy necessary to grind coals to the same fineness are determined by the number of revolutions of the mill required to reduce the sample to a fineness of 80 percent passing a 200-mesh sieve. Coal ground to 200-mesh size is removed in increments of 10 percent by stopping the mill and screening out the undersize at predetermined intervals. This procedure simulates commercial grinding practice, in which the finished product is removed continuously by a current of air. The grindability index is obtained by dividing the number of revolutions into the factor 50,000. By this procedure, the relative ease of grinding each coal is rated as a percentage of a hypothetical standard coal requiring 500 revolutions.

The results of a comparative study of grindability methods conducted under the auspices of the American Society for Testing Materials were described by Selvig.⁴⁷ Five laboratories cooperated by making grindability tests of five coals covering a wide range in grindability, using the Cross, F.R.L., Hardgrove, and ball-mill methods. The ball-mill and Hardgrove tests were found to be superior in precision and upon this basis were selected as tentative standards of the society.⁴⁸ A subsequent investigation⁴⁹ showed that the C.I.T. roll test did not give results that were reproducible even in the same laboratory.

The principal advantage of the Hardgrove method lies in the rapidity with which tests can be made; a major disadvantage is that it requires an expensive

grinding machine. In contrast, the ball-mill method utilizes only inexpensive apparatus, part of which is standard laboratory equipment, but duplicate determinations require about 4 hours longer than duplicate Hardgrove tests. The relative advantages of time required and cost of equipment are easily weighted, but the merits inherent in the basic principle of the two methods are more difficult to evaluate. It has been shown clearly⁴⁹ that in grinding only part of the coal the Hardgrove test is susceptible to selectivity: that is, only the softer components of the coal are crushed, leaving unground the harder particles that would have to be treated in commercial grinding. This source of error is eliminated in the ball-mill method by grinding all the sample to finished size.

Black⁵⁰ pointed out an apparent anomaly in the results of both standard grindability tests. The impurities associated with coal, and therefore coals containing such impurities, are sometimes higher in grindability than the corresponding clean coal, yet pyrite, sandstone, and many shales generally are regarded as relatively hard and tough, therefore as comparatively difficult to pulverize. Discussion of Black's paper brought out the point that the higher specific gravity of the impurities offsets the effect of their greater hardness; moreover, a commercial pulverizer actually has as great a capacity in tons per hour on hard, heavy material of given grindability as on softer, lighter material of the same grindability index.

RELATION BETWEEN GRINDABILITY AND RANK

A general relationship exists between the grindability of coal and its rank. Figure 1 shows grindability indexes plotted against dry, mineral-matter-free fixed carbon for

⁴⁷ Selvig, W. A., *U. S. Bur. Mines, Rept. Investigations* 3301 (1936), 16 pp.

⁴⁸ *Am. Soc. Testing Materials, Standards*, 1939, Pt. III, 562-5, 566-9.

⁴⁹ Yancey, H. F., and Geer, M. R., *Trans. Am. Inst. Mining Met. Engrs.*, 119, 353-69 (1936).

⁵⁰ Black, C. G., *Trans. Am. Inst. Mining Met. Engrs.*, 119, 330-52 (1936).

the higher-rank coals and against moist, mineral-matter-free British thermal units for the coals of lower rank. The grindability indexes, indicated by open circles, were obtained by the ball-mill method, and the filled circles represent Hardgroove tests converted to their approximate ball-mill equivalents. These data were drawn prin-

coals in Fig. 1 include samples from nearly every coal-producing state.

The coals that are easiest to grind are found in the medium- and low-volatile groups; they are decidedly easier to grind than the coals of high-volatile bituminous, subbituminous, or anthracitic rank; however, the relationship between grindability

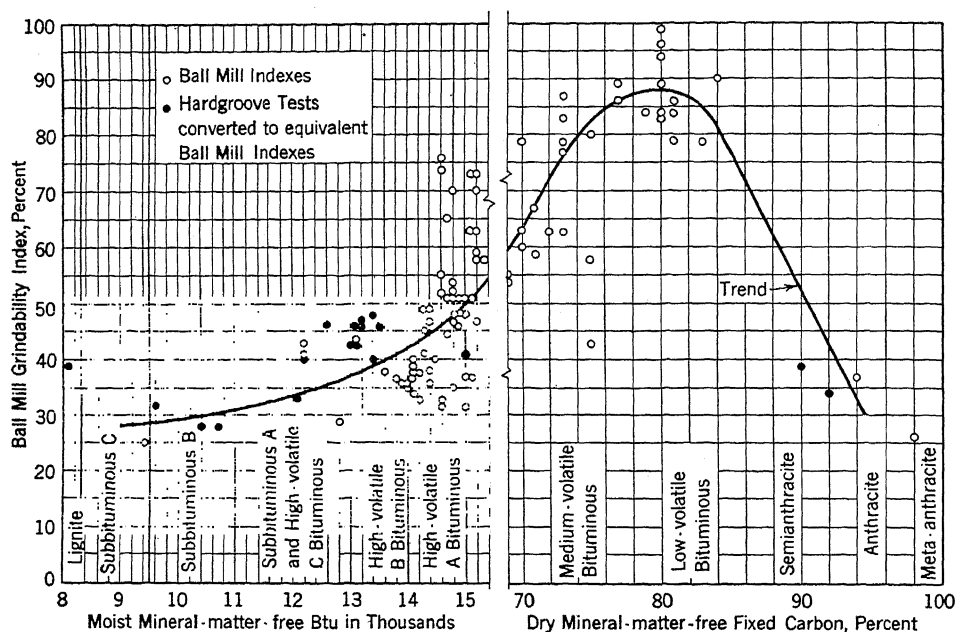


FIG. 1. Relation between grindability and rank.

cipally from publications of the Bureau of Mines,⁵¹ and of Brunjes,⁵² supplemented by reports of Gilmore and Nicolls²⁶ and the Babcock and Wilcox Company.⁵³ The

y, H. F., and Geer, M. R., *U. S. Bur Mines, Rept. Investigations* 3409 (1938), 9 pp. Hertzog, E. S., and Cudworth, J. R., *ibid.*, 3382 (1938), 8 pp. Hertzog, E. S., Cudworth, J. R., Selvig, W. A., and Ode, W. H., *U. S. Bur. Mines, Tech. Paper* 611 (1940), 58 pp.

⁵² Brunjes, H. L., *Trans. Am. Inst. Mining Met. Engrs.*, 119, 371-4 (1936). Brunjes, H. L., *Combustion*, 11, No. 11, 31-4 (1940).

⁵³ *The Babcock and Wilcox Co., New York, Bull.* 3, 241 (1938).

and rank is far too approximate to permit grindability to be estimated from the analysis of a coal. Coals of similar analysis often differ greatly in grindability, as indicated by the spread of points in Fig. 1.

The relationship between the petrographic composition of coal and its friability has already been mentioned. A similar relationship exists between petrographic composition and grindability. McCabe⁵⁴ separated the vitrain, clarain, and

⁵⁴ McCabe, L. C., *Trans. Am. Inst. Mining Met Engrs.*, 139, 382-3 (1940).

durain from a sample of Illinois coal and determined the grindability of each constituent. The ball-mill grindability index of the vitrain was 47 percent, that of the clarain 40 percent, and that of the durain only 16 percent. Fusain gave an index of 121 percent; however, the suitability of the determination for such soft material

for some coals as much as 15 units higher. For other coals the grindability of both coarse and fine sizes was substantially the same, and for a few coals the grindability was higher for the material of larger size. This variation in grindability with size reflects the segregation of petrographic constituents and impurities.

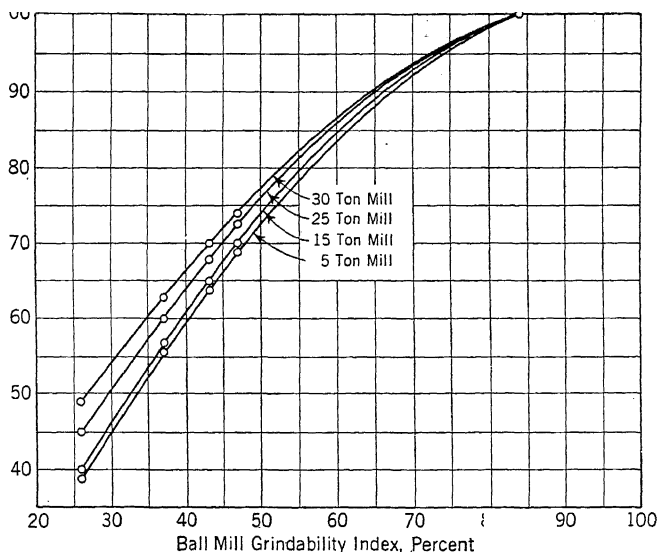


Fig. 2. Relation between pulverizer capacity and grindability for various sizes of ball mills, according to Frisch and Foster.⁵⁵

has never been demonstrated. Thus, the various constituents of the same coal varied over a wider range of grindability than that exhibited by the entire group of coals shown in Fig. 1. Such differences in grindability allow the petrographic constituents to be separated in the percussion mill described by Lehmann and Hoffmann.⁵⁵

Gilmore and Nicolls,²⁸ in tests of three sizes of 39 coals, found that for about half the coals the finer sizes were higher in grindability than the coarser material—

⁵⁵ Lehmann, K., and Hoffmann, J., *Brennstoff-Chem.*, 13, 21-9 (1932).

RELATIONSHIP BETWEEN GRINDABILITY AND PULVERIZER PERFORMANCE

The grindability test serves primarily as a means of estimating how various coals affect the capacity of commercial pulverizers. It has long been known that the capacity of a pulverizer is related to the grinding properties of the coal pulverized, but only the relatively recent advent of laboratory grindability tests has made it possible to quantify this relationship. The fact that so little information is available to show the correlation between grindability and mill capacity is attributable to the

newness of the standardized grindability tests and to the many factors that must be considered in making such a correlation.

Frisch and Holder⁵⁶ have shown that the capacity of a pulverizer, in addition to depending on grindability, is influenced by the size of coal in the feed, by its moisture content, by the degree to which the grinding elements are worn, and particularly by the fineness of grinding. These investiga-

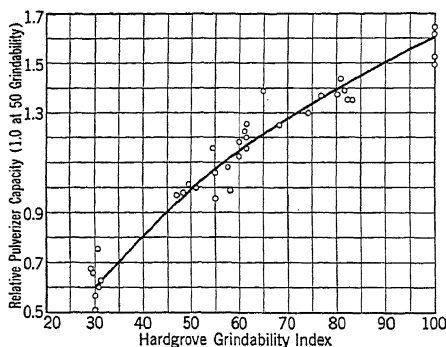


FIG. 3. Relation between pulverizer capacity and grindability for ring-and-ball-type pulverizers, according to Hardgrove.⁵⁹

tors found that when the various factors are taken into account, that is, when pulverizer tests are reduced to a comparable basis, mill capacity is closely related to grindability. Rosin and Rammler⁵⁷ have made exhaustive studies of the performance of coal pulverizers and have reduced their results to the form of a complete mathematical analysis of the principal factors that affect pulverizer capacity.

In a recent report Frisch and Foster⁵⁸

⁵⁶ Frisch, M., and Holder, G. C., *Combustion*, 5, No. 1, 29-34 (1933).

⁵⁷ Rosin, P., and Rammler, E., *Berichtfolge des Kohlenstaubausschusses des Reichkohlenrates*, Nos. 3 (1926), 14 pp., 9 (1927), 35 pp., 12 (1928), 15 pp.; *Arch. Wärmewirt.*, 7, 54-7, 81-5 (1926), 8, 69-73, 109-15 (1927); *Braunkohle*, 26, 261-8, 286-93 (1927).

⁵⁸ Frisch, M., and Foster, A. C., *Proc. Am. Soc. Testing Materials*, 1937, Pt. II, 441-66.

have presented data showing the correlation between laboratory grindability values and the capacities of Hardinge-type ball mills. Figure 2, prepared from their report, indicates the relationship between the capacity tests of four sizes of ball mills, properly adjusted to a comparable basis, and ball-mill grindability indexes. The curves in Fig. 2 indicate that although mill capacity and grindability are related they are not directly proportional; that is, a coal having a grindability index twice that of another cannot be ground with twice the capacity. Moreover, the relationship between capacity and grindability differs for various sizes of the same type of pulverizer and doubtless for each type of pulverizer. Upon this basis, Frisch and Foster concluded that grindability tests can be used to predict the capacity of a pulverizer on coals of known grindability only when the capacity-grindability relationship for that particular pulverizer has been determined by correlative tests and when the other factors influencing capacity are considered.

Hardgrove⁵⁹ has determined the relationship between pulverizer capacity and grindability for ring-and-ball-type pulverizers, and his results are shown graphically in Fig. 3. His curve relating capacity and grindability is similar in form to the curves shown in Fig. 2 for ball mills. Hardgrove blamed incomplete scavenging in mills treating softer coals for the fact that pulverizer capacity is less on the softer coals than would be represented by a direct proportionality between grindability and capacity. He thus concluded that in mills having more perfect scavenging the capacity would be more nearly proportional to grindability.

⁵⁹ Hardgrove, R. M., preprint for presentation at the spring meeting of the American Society of Mechanical Engineers, Chicago, June 27, 1933.

Schultes and Goecke⁴¹ have advanced the opinion that the relationship between grindability and mill capacity is influenced to such an extent by the type of grinding action employed that it should be possible to eliminate the effect of grindability by choosing the best type of mill for each type of coal. This opinion may be ex-

treme, but it serves to emphasize the necessity for careful correlation between grindability tests and mill performance.

An excellent review of the literature on the grinding of coal has been prepared by Heywood.⁶⁰

⁶⁰ Heywood, H., *Combustion Appliance Makers Association (London)*, Document No. 1657, 1938.

CHAPTER 6

PLASTIC, AGGLUTINATING, AGGLOMERATING, AND SWELLING PROPERTIES OF COALS *

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A critical review of the numerous test methods that have been devised for measuring the "plastic" and "swelling" properties of bituminous coking coals and a practical evaluation of the test data have been long needed. In this survey of the various classes of test methods the constant aim has been to describe the test principles employed and the usefulness of the data obtained in their relation to the complex problem of coking bituminous coals, rather than to stimulate unduly a controversial criticism of the merits and limitations of any particular class or of individual test methods devised by different workers. The whole problem has been quite difficult because of the almost total lack of accepted test standards and specifications. Detailed descriptions of apparatus and test procedures of published papers reviewed in this chapter are given in the *U. S. Bureau of Mines Bulletin*¹ entitled "Plastic and Swelling Properties of Bituminous Coking Coals."

DEFINITIONS OF TERMS

Probably in no other branch of industry has there been introduced such a wide

variety of terms intended to describe or define the many phenomena observed under various laboratory test and plant conditions as has appeared in the field of coal technology. This situation has resulted not so much from lack of intelligent thought as from the difficulties in describing adequately and interpreting correctly in simple and concise language the complex behavior of coal when heated. Accurate measurements of the physical and chemical properties of any heterogeneous material are difficult, but the problem becomes far more laborious for coal, whose already complex composition is changed quite markedly during test conditions involving heating. The difficulty of controlling variables and of determining or even predicting the changes that take place can seldom be met entirely. For these reasons, most of the terms used to define certain observations made during the testing of coals must, of necessity, incorporate factors that describe essential test conditions pertinent to those observations. Many of the special terms used by investigators, whose work has been reviewed, will be defined when first introduced. Because of their frequent use, the meaning of the terms "plasticity," "swelling," "swelling pressure," "agglutinating value," and "agglomerating value" will be explained here.

* Published by permission of the Director, Bureau of Mines, United States Department of the Interior.

¹ Brewer, R. E., *U. S. Bur. Mines, Bull.* 445 (1942), 260 pp.

Plasticity. Among workers in coal technology, the widely used term "plasticity" of bituminous coking coals is perhaps better understood than it is capable of clear-cut definition. One of the best is the following definition, which was given by Mott and Wheeler: ² "The plasticity of coal is a complex phenomenon which appears to be induced primarily by the pressure of gases causing surface flow at the moment when, under the action of heat, the molecules at the surface have attained a degree of freedom comparable with that obtaining in a liquid." The plasticity of coal does not precede the evolution of "volatile matter," although most of the volatile may be actually evolved while the coal is plastic.

Swelling and Swelling Pressure. The characterization of the process of increasing the volume of a coal charge by heating and of its aftershrinkage, if any, has been greatly confused through loose and interchanged use of the terms "swelling" and "swelling pressure." In some instances, only a linear change, usually in the vertical direction, of the original dimensions of the confined heated coal charge was intended; in others, the concept of an increase in pressure within the charge was denoted. Worthwhile distinctions made by Damm ^{3, 4} were that *swelling* (Blähen) signified a volume change that takes place during heating of many coals under such conditions that the softened coal can *expand freely* in a direction perpendicular to the heating surface, whereas *force* (Treiben) denoted the pressure that the softened coal mass

frequently exerts when it is *obstructed from free expansion*. The magnitude of the *degree of free swelling* (Blähgrad) can be expressed numerically in convenient linear units, or in percentage of the original coal volume. *Swelling pressure* or *expansion pressure* (Treibdruck) is usually expressed in some *pressure unit per unit area*, such as kilograms per square centimeter or pounds per square inch. Shimomura ⁵ has suggested the more literal translation of "Treibdruck," namely, "driving pressure," as more suitable and less confusing than the commonly used equivalent English term "swelling pressure" or "expansion pressure."

Agglutinating Value. The dictionary definition of the word "agglutinate" is "to unite or cause to adhere, as with glue or other viscous substance; to unite by adhesion." The "other viscous substance" in the case of caking and coking coals is formed during the heating of the coal in the absence or near absence of air. Under procedures for determining the agglutinating value of coals this viscous substance, heavy tar, is distributed around the sand grains (or other inert material) used. When the sand-coal mixture is cooled, the viscous substance solidifies and binds the sand and coal residue in a compact mass. *The agglutinating value, then, is a measure of the binding qualities of a coal and is an indication of its caking or coking characteristics.*

Agglomerating Value. The terms "agglutinating" and "agglomerating" have been frequently used in a synonymous sense. More recently, "agglomerating value" has been properly restricted to describe the results of coke-button tests in which no inert material is heated with the coal sample.

⁵ Shimomura, A., *J. Inst. Fuel.*, **13**, 247-56 (1940).

² Mott, R. A., and Wheeler, R. V., *The Quality of Coke*, Chapman and Hall, London, 1939, pp. 11-2.

³ Damm, P., *Arch. Eisenhüttenw.*, **2**, 59-72 (1928); *Glückauf*, **64**, 1073-80, 1105-11 (1928); *Fuel*, **8**, 163-77 (1929).

⁴ Damm, P., *Brennstoff-Chem.*, **10**, 65-7 (1929).

RHEOLOGICAL PROPERTIES OF BITUMINOUS COALS

The study of the flow of matter, which to avoid circumlocution is now called rheology, has attracted the attention of scientists for many centuries. However, in spite of many excellent studies from which have come much valuable knowledge and some fundamental theories on how the association between molecules affects the properties of materials, the difficulties inherent in the subject are so complex that but little progress has yet been made in the formulation of entirely adequate definitions. The best thought of able investigators in the fields of both pure and applied rheology is embodied in the recently revised "Tentative Definitions Relating to Rheological Properties of Matter."⁶ These definitions are stated as follows:

Consistency. That property of a body by virtue of which it tends to resist deformation.

Plasticity. That property of a body by virtue of which it tends to retain its deformation after reduction of the deformation stress to its yield stress.

Elasticity. That property of a body by virtue of which it tends to recover its original size and shape after deformation.

Liquid. A substance which undergoes continuous deformation when subjected to shearing stress.

Simple Liquid. A liquid in which the rate of shear is proportional to the shearing stress. The constant rate of shearing stress to rate of shear of a simple liquid is the *viscosity* of the liquid.

Complex Liquid. A liquid in which the rate of shear is not proportional to the shearing stress.

Solid. A substance which undergoes permanent deformation only when subjected to

shearing stress in excess of some finite value characteristic of the substance (yield stress).

Plastic Solid. A substance which does not deform under a shearing stress until the stress attains the yield stress, when the solid deforms permanently.

Elastic Solid. A substance in which, for all values of the shearing stress below the rupture stress (shear strength), the strain is fully determined by the stress regardless of whether the stress is increasing or decreasing.

The rheological term plasticity, among others, has no definite dimensions and no exact definition. In the words of Blair,⁷ "Although plasticity cannot yet be defined in absolute units, yet like honesty, it is 'although undefinable, associated with certain properties.'" The word implies a low viscosity, at least at higher stresses, combined with a yield value such that the shape can be retained under the stress of gravity.

The situation with respect to definitions exists for nearly all kinds of natural and manufactured materials but is particularly true for the complex heterogeneous substance, bituminous coal, whose behavior during coking has frequently even raised the moot question as to whether coal is a plastic material. However, there is abundant evidence that bituminous coal, when heated under appropriate conditions, may exhibit, at times, plastic, viscous, and elastic flow, and very often complex combinations of two or all three of these types of flow. The commercial coking of bituminous coals may be regarded as a consequence of their plastic flow as a whole, by which the interspaces are filled and the particles coalesce by surface-tension effects. It is evident from the law of plastic flow that there can be no flow without enough net pressure in, or on, the coal charge.

⁶ Am. Soc. Testing Materials, Preprint, Report of Committee E-1, 1940, p. 26; 1940 Supplement to Am. Soc. Testing Materials Standards, Pt. III, p. 557, 1940.

⁷ Blair, G. W. Scott, *An Introduction to Industrial Rheology*, The Blakiston Co., Philadelphia, 1939, p. 62.

EVIDENCE OF PLASTICITY IN COAL

Historically, the first evidence of plasticity in bituminous coals undoubtedly was first observed directly in a coal-fire fuel bed. Proof that there is a surface flow of the heated coal during the formation of coke has been demonstrated by numerous investigators. Two such investigations will serve to illustrate the evidence of plasticity in both the particle and in a briquetted column of coal particles.

Davies and Mott⁸ found that a 1-inch cube of solid Parkgate Seam coal, when heated to a temperature of 360 or 380° C in an inert atmosphere, swelled without cracking. Application of pressure to the cube heated to 360° C, when a 100 percent increase in volume had occurred, or to a similar cube heated to 380° C, when a 124 percent increase in volume had taken place, caused the coal specimens to contract. The first cube ruptured under the high pressure, whereas the second cube under similar treatment contracted readily to a residual swelling of 38 percent, but without rupture. The second cube retained its regular shape and pore structure, but the pores had reorientated themselves parallel to the bedding plane of the coal.

Mott and Wheeler⁹ made a number of pellets from Two Foot Nine Seam coal from South Wales by briquetting samples of 60-mesh size under a pressure of 3 tons per square inch. This coal contained 89 percent carbon and 4.6 percent hydrogen. It showed softening at 404° C and swelling over the temperature range 444 to 464° C in the Sheffield Laboratory Coking Test. The polished top surface, produced by briquetting, was removed from the reference pellet *A* with Carborundum powder, and

any resulting scratches with finer Carborundum passing a No. 40 Whatman filter paper. This pellet, after polishing with rouge on a leather (500 strokes being given), was then photographed at 140 magnification. The microphotograph of this reference (unheated) pellet *A* plainly revealed the outlines of the original particles of coal.

Similar pellets were prepared and heated to a series of temperatures, 435, 445, 460, and 470° C, at a rate of 1° C per minute, cooled, and treated in the manner described for the unheated reference pellet. In pellet *B*, heated to 435° C, the outlines of the original particles, although less clear than in pellet *A*, were still evident. In pellet *C*, heated to 445° C (swelling temperature, 444° C), the outlines of the original particles of coal were almost completely obliterated, and an almost continuous polished surface was obtained. This pellet, after etching for 1 minute with concentrated sulfuric and chromic acids to remove the polished surface, showed that, below the surface which had been subjected to external pressure, no "fusing" together of the particles had been induced by internal gas pressure, and the outlines of the individual particles were still evident. In other words, the continuity of the surface of pellet *C* was due to surface flow induced by external pressure, and the surface became "liquidlike." The molecules on the surface, being bound only on the side beneath the surface, had a degree of freedom associated with the liquid rather than the solid state.

Pellet *D*, heated to 460° C, also showed surface flow, and a part of the surface appeared to be more liquidlike than in pellet *C*. After etching, the outlines of the individual coal particles below the original polished surface in pellet *D* had been entirely lost, owing to internal changes.

⁸ Davies, R. G., and Mott, R. A., *Fuel*, **12**, 330-40 (1933).

⁹ See pp. 334-5 of ref. 2. See also Mott, R. A., *Fuel*, **12**, 412-8 (1933).

Some of the surface flow could, therefore, be due to internal gas pressure. Pellet *E*, heated to 470° C, showed large pores at the surface; at higher temperatures the continuity of the surface was even more broken.

The limiting temperature at which coal could no longer be caused to flow readily by surface pressure, therefore, could not be determined. It may be concluded, however, that surface flow produced by a light external pressure is more readily produced in coal which has been heated to a temperature within the plastic range, and therefore, that, with the high gas pressure available during this range, surface flow by gas pressure can be held to account for the phenomenon of plasticity during the apparent fusion of coal.

EVALUATION OF COKING PROPERTIES OF BITUMINOUS COALS

The different types of test methods that have been used in evaluating the ability of various bituminous coals to produce commercial coke may be divided conveniently into two groups: (1) methods that involve individual separations of certain constituents or portions of the coal or of its products of carbonization, and (2) methods that give some insight into the coking behavior of the coal as a whole. Allowing for some overlapping in the two groups, the first group includes proximate analyses, ultimate analyses, crucible coking tests, methods of distillation, extraction by solvents with heat and with or without pressure, measurements of the degree of swelling caused by certain liquids at room temperatures, float and sink analyses, and microscopic examination of the petrographic constituents. The second group includes determinations of the softening behavior, the course of degasification, swelling power, expansion pressure, and aggluti-

nating, agglomerating, and permanganate numbers.

Each type of test has contributed something to the general knowledge of the properties and composition of coal, but only a few of these tests furnish data from which a critical and active pursuit in the development of new fundamental knowledge can be advanced for the elucidation of the chemistry of coal. Present knowledge of the chemistry of coal is still more qualitative than quantitative, and combinations of data obtained from several of the above-listed methods of test are necessary to evaluate the coking properties of individual bituminous coals. This situation is true because of the many variables that enter into the coking process and the difficulties of maintaining experimental conditions so that these variables act in the same or closely similar manner in a given test method. It will be noted that both groups of methods include tests for determining, directly or indirectly, the plastic and swelling properties of bituminous coking coals.

CLASSIFICATION OF TEST METHODS

Most of the publications describing determinations of plasticity and other closely related properties of bituminous coals include at least one bibliographical reference to earlier work, and some contain reviews of certain of these earlier publications. Comparisons of the descriptions given in the reviews with those found in the original source publications, however, often show a more or less confused conception of the particular principle actually used in individual methods of test. This confusion is due, in part, to certain similarities in the apparatus and procedures in two given methods. Sometimes several different principles have been combined in individual methods. Therefore, a somewhat arbitrary

classification representing the more prominent of the overlapping principles had to be chosen.

Certain practical measurements have been made by a number of empirical methods, employing several distinctly different basic principles in their procedures. As an outgrowth of these conventional methods, numerous modifications have been introduced into the individual original methods with resulting real or fancied improvements in the apparatus and procedures. Data obtained in most of these conventional methods are of such a nature that the problem of interpretation in terms representing the concepts of the rheologist is extremely difficult. Absolute methods of test often yield more fundamental information than methods involving other variables, and they should be encouraged. However, because of the great refinements in apparatus and experimental technique necessary in the absolute methods, and because the data obtained, being limited to short ranges of temperature, are therefore necessarily less applicable to commercial coking problems, these methods have not been widely developed or adopted.

The present classification of methods for measuring the plastic and swelling properties of bituminous coking coals has been made according to the general principles of the methods concerned. For convenience, the methods reviewed have been classified broadly into nine groups as follows:

- I. Absolute methods of measuring plasticity of coal.
- II. "Direct observation" test methods.
 1. Macroscopic and microscopic tests.
 2. Absorption of cold pyridine.
- III. Agglutinating and free swelling (*Blähen*) test methods, coal under no added load.
 1. Laboratory crucible and tube tests.

- a. Agglutinating value tests on inert material plus coal.
 - b. Coking or caking tests on coal alone.
 - c. Agglomerating index of coal on coal alone.
2. Large-scale box and muffle tests.
- IV. Dilatometer and penetrometer test methods, coal under no load or known added load.
- V. Gas flow or Foxwell test methods.
- VI. Torsional or resistance of mass to shear test methods.
- VII. Extrusion test methods.
- VIII. Swelling pressure or expansion pressure test methods.
- IX. "Plastometric investigations" on Russian (U.S.S.R.) coals.

ABSOLUTE METHODS OF MEASURING PLASTICITY OF COAL

Absolute methods permitting precise and reproducible measurements of the magnitude and distribution of shearing stresses in the coal specimen when heated at elevated temperatures have been devised by Seyler in England and by Griffin and Storch in the United States.

Seyler¹⁰ studied the physical behavior of coal when heated rapidly and uniformly to a definite temperature in an apparatus in which quantitative measurements were claimed. The contraction or expansion of a small upright cylinder of heated coal, contained in a tubular space of slightly larger diameter, was observed from the vertical movement of the coal before a stationary glass index of a graduated dilatometer rod that rested on the top end of the cylinder.

The cylinder consisted of solid coal or of coal particles of uniform size (or limit of variation), that had been compressed uniformly to a definite apparent specific gravity. The cylinder was small enough to

¹⁰ Seyler, C. A., *Proc. S. Wales Inst. Engrs.*, **47**, 9-15 (1931); *Colliery Guardian*, **142**, 401-4, 488-90, 577-9 (1931).

insure uniform and rapid heating. After the dimensions of the cylinder had been determined accurately, it was set centrally on the flat bottom of a straight-walled, iron heating tube. The top end of the cylinder supported a dilatometer rod, whose head gave a small clearance with the wall of the heating tube. The rod could be loaded, by changing the weights on a counterpoise pan, to exert any desired vertical pressure. The annular space between the coal and the wall of the heating tube permitted a decrease in length (contraction) of the coal cylinder as it softened during the test. Thus arranged, only the top and bottom ends of the cylinder were in contact with apparatus parts at the start of the test.

To carry out the test, the apparatus was prepared and the covered furnace tube containing the coal was heated rapidly to the desired temperature by means of a well-stirred, fusible metal bath. The temperature of the bath was measured by a thermometer. The vertical movements of the graduated dilatometer rod were read with reference to the stationary glass index. As the coal cylinder contracted in length its cross-sectional area increased, and, therefore, the pressure applied on its top area decreased. To obtain comparable rates of deformation per unit of length of the cylinder at any moment and constant pressure on the cylinder, cylinders of identical original length were used. The percentage contraction of the cylinder was plotted against the time in minutes. The slope of the curve measured the velocity of deformation in percentage of the original length of the cylinder per minute of time.

Rates of Deformation under Different Loads. Cylinders of Busty Seam vitrain coal were heated under increasing loads to a temperature well above the softening

point of the coal (325°C), but below its intumescent, or swelling, point (not given). The percentage contractions of the original length of the cylinders when plotted as ordinates against time in minutes as abscissas gave a family of curves. These curves showed that the rate of contraction increased with the pressure applied, and this increase was of the same order as that of the pressure, at any rate in the earlier stages, say at 3 percent contraction. In contrast to the behavior of substances like pitch at temperatures below their decomposition points, the rate of deformation of the coal under a constant pressure decreased as the contraction proceeded until it finally became zero and the flow ceased. Seyler believed that the cessation of flow was not due to the loss of the property of flow under pressure but to the development of a resistance that is probably of the nature of a back-pressure produced by gases of decomposition from the heated coal. The resistance to deformation, which increased with the total extent of the contraction, acted in the opposite direction to the applied load and tended to produce expansion. If the load was diminished, temporary expansion took place until the total contraction was reduced to correspond to the reduced load. Seyler cited as confirmatory evidence the fact that, when ammonium carbonate is mixed with pitch and heated, the gases given off by decomposition of the ammonium carbonate at the softening temperature of the pitch cause the pitch to intumesce, or swell.

If the temperature attained by the coal was high enough, the equilibrium obtained after a certain time with any given pressure was followed by intumescence or swelling, and the coal began to expand. This expansion was attributed to the fact that the gases formed by decomposition of the coal cannot escape fast enough.

Plastic Flow of Coking Coals. The fact that the rate of deformation increased with the pressure applied and that in the absence of pressure there was no flow indicated that the phenomenon was one of plastic flow rather than of fusion. Cylinders cut from solid sections of petrographically uniform coal behaved in the same way as those made by compression of coal particles, not only quantitatively but also according to the laws that govern the rate of deformation. Cylinders of coal in both conditions swelled at about the same temperature. Hence, the resistance to escape of gases from the coal must have been caused by the interstices between the colloidal particles of the coal itself and not by the voids between the granules of which the compressed coal was composed. Moreover, a good coking coal, when suitably heated, may be drawn out into fine threads just like a plastic substance.

To compare different cylinders, the rates of flow under different pressures at a constant length of cylinder were determined. The data for the Busty Seam vitrain coal at a temperature of 361° C were replotted, using loads in grams as ordinates and rates of contraction as abscissas. The initial stages being neglected, the total contraction agreed with the law of plastic flow. The family of graphs, representing different given lengths of the cylinder, up to a load of 50 grams, was a series of parallel straight lines that intercepted the ordinate axis at different points. Under these conditions the pressure was the intercept on the ordinate axis and a true yield value.

The method outlined by Seyler for converting his data into cgs units is not clear. Furthermore, a number of the conclusions given in his two papers are inconsistent. These earlier views of Seyler have been modified somewhat and extended as a re-

sult of later work,¹¹ details of which have not been published. In the latest of these,¹¹ Seyler says, "I hope to publish at the first opportunity a detailed account of the work which has been done by myself and Mr. Harding Edwards with the aid of the Fuel Research Board." A lucid account of the work of Seyler on the relationship of plasticity to certain other properties of bituminous coal conducted during the last ten years with complete literature references to the work of others upon which he bases his interpretations of the rheological properties of bituminous coking coals would be a welcome contribution.

The apparatus of Seyler, though correct in principle, did not preclude the possibility of eccentric loading. An eccentric load, very small in absolute units because of the small size of the coal specimen, would cause large variations in the lateral distribution of the shearing stress.

Griffin and Storch¹² made provision in their apparatus to center the load very accurately. All forces on the coal specimen other than that of the net load to be applied were eliminated by means of an ingenious loading arrangement.

Figure 1 is a diagram of the plastometer assembly drawn to scale, and Fig. 2 a detailed drawing with dimensions. For a complete description the reader should consult the original paper.*

Cylindrical pellets were formed by compressing minus 200-mesh coal in a mold kept at 300° C to a pressure of 7,050 kilograms per square centimeter. Their computed apparent densities ranged from 1.27 to 1.29. Deformation of a pellet during

¹¹ Seyler, C. A., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board Repts.*, 1933, 39-40, 1935, 41-2, 1936, 53-4, 1937, 39-40, 1938, 65-7; *J. Inst. Fuel*, 11, 301-3 (1939).

¹² Griffin, H. K., and Storch, H. H., *Ind. Eng. Chem., Anal. Ed.*, 9, 280-6 (1937).

heating was observed by means of a low-power microscope.

Pellets of a blend of 80 percent of Pittsburgh Seam and 20 percent Sewell Seam were loaded as desired, and the same

meter and appears to be independent of loads above this value; and (3) the slope of time versus changes in length curves, before and after the maximum length of

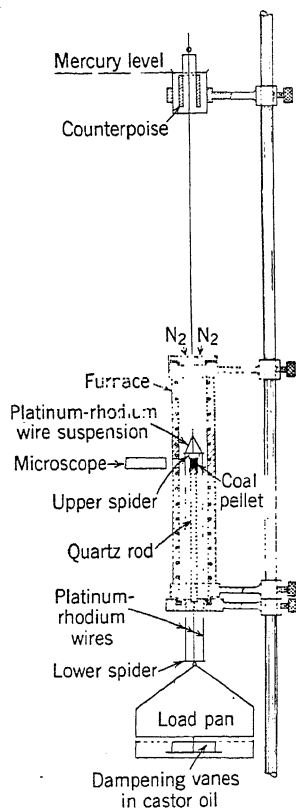


FIG. 1. Plastometer assembly.^{1,2}

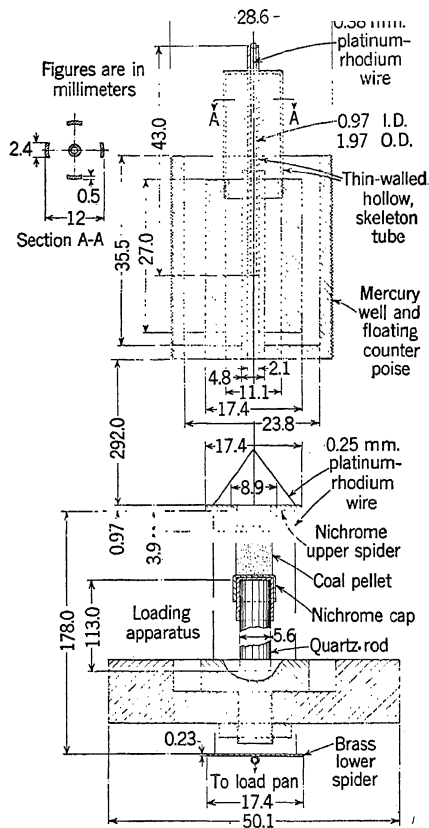


FIG. 2. Detailed drawing of plastometer.^{1,2}

load was maintained throughout the test. The heating schedule was about 7°C per minute up to 350°C , and about 1°C per minute thereafter. The curves of Fig. 3, showing deformations plotted against time, indicate three striking facts: (1) the temperature of initial contraction decreases with increasing load; (2) the maximum increase in length decreases with increasing load up to 600 grams per square centi-

the pellet is reached, is about the same for all loads. The first fact is not the result of improved thermal contact of the nichrome caps on the ends of the pellet, because tests with Pyrex caps at corresponding pressures did not change the respective initial contraction temperatures. The decrease in maximum expansion with load might have been due to an increased rate of filling the voids by closer packing

of wetted grains of material. Beyond about 600 grams per square centimeter the frictional resistance accompanying such closer packing may be great enough to make further deformations almost independent of load. The third fact shows that continuous deformation proportional to load did not exist under the test conditions.

rate curve indicated that the deformations were elastic rather than plastic.

Both the blend of coals and the mixture of Alma Seam coal and electrode carbon under the test conditions showed very transient plastic properties, the life period being of the order of 1 minute at 460° C. Measurable deformations were character-

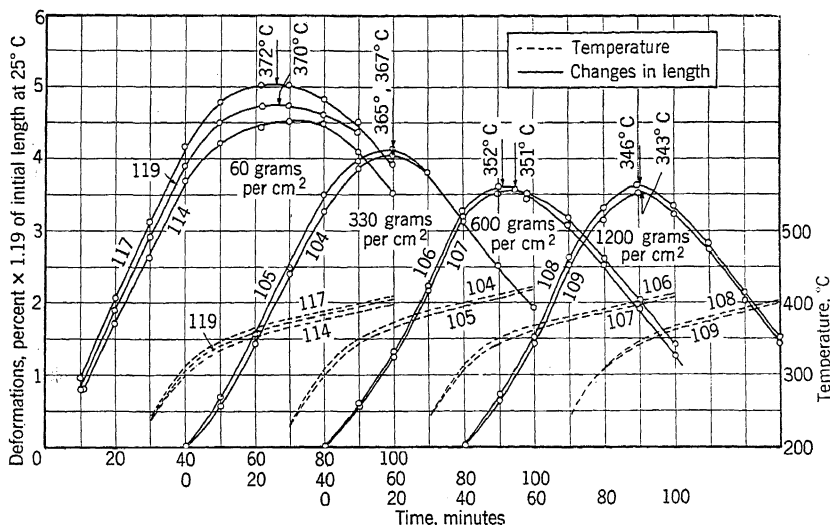


FIG. 8. Heating experiments with coal 30, a blend of 80 percent Pittsburgh Seam and 20 percent Sewell Seam coals.¹²

With rapid heating (within 3 to 4 minutes) to temperatures of 410 to 475° C, plastic deformations of the coal alone were too fast to be measurable. Measurements of deformations proportional to the load at 410° C, therefore, were obtained on pellets made of coal 30 and Alma Seam coal each with 20 percent additions of 200- to 220-mesh electrode carbon. Deformations per minute for stated time intervals within a total time of 40 minutes after the maximum length of the pellet had been reached showed increased deformation with load and decreased deformation with time. An abrupt change in slope of the deformation-

ized as those of an elastic solid whose elasticity was being rapidly destroyed by chemical decomposition. The Alma Seam coal was definitely more deformable at 410° C than the blend of coals. This is in qualitative agreement with data obtained on these coals by the Davis plastometer test method.

The solid plus oily bitumens obtained upon pressure extraction of the blend of coals with benzene were pelleted. Plasticity was determined at 120° C under pressures of 20 to 250 grams per square centimeter. The decrease in length of pellet with time, which was observed almost im-

mediately and was continued throughout the time of application of the load, was linear, showing that the bitumens behaved as a truly plastic substance.

DIRECT-OBSERVATION TEST METHODS

The direct-observation test methods include macroscopic and microscopic tests of the heated coal, and absorption or adsorption of reagents by the coal with resulting swelling at ordinary temperatures.

MACROSCOPIC AND MICROSCOPIC TEST METHODS

Lessing¹³ was probably the first to make direct laboratory observations of the melting and reagglomeration of heated coal. Tests carried out in a clear quartz glass tube gave little promise that much information could be obtained directly in this manner.

Mott¹⁴ studied the effect of heat on large pieces of 17 different coals ranging in carbon content from 78.9 to 92.2 percent (dry, ash-, and sulfur-free basis). The samples included 9 bright coals (clarains, one an anthracite), 6 hard or dull coals (durains), and 2 mixtures of "brights" and "hards." One-inch cubes were cut out with a hack saw, measured accurately, and photographed. The cubes were placed in a large silica tray which was inserted in a tightly closed electric muffle through which oxygen-free nitrogen was passed during the experiment. The temperature was raised fairly rapidly to 300° C, thereafter at 1° C per minute up to 600° C. The cokes were allowed to cool in an inert atmosphere, measured, and photographed. They were then sectioned by Rose's method,¹⁵ i.e., set in plaster of Paris, sectioned with a Carbo-

rundum cutting wheel, and polished with various grades of emery, a final polishing being given with alumina. The sections were then examined microscopically and photographed at right angles to the bedding plane of the original coal. The porous structure of the cokes was shown in the sections.

Except for the anthracite, the swelling of the bright coals decreased fairly regularly with decreasing carbon content and was always greater at right angles than in the direction parallel to the bedding plane of the coal. Pore structure was less well defined, in general, in the lower-rank coals. Distortion and disruption of the pores indicated that appreciable gas pressures were associated with apparent liquefaction. Fracture cracks in the cokes denoted release of gas pressure developed during the plastic state of the coals. The structure of the cokes prepared from the "hards" signified that either only small gas pressures were developed during the critical stages of coke formation or that the developed pressures were easily released.

Mott and Shimmura¹⁶ subjected a number of moderate and inferior coking coals to methods of examination similar to that just described. Particular attention was given to the effect of the rate of heating. The coals were from 9 seams—4 from a Yorkshire colliery and 5 from a Derbyshire colliery—and included 9 "brights" (clarains) and 5 "hards" (durains). All the "brights" were high-volatile coals with carbon contents ranging only from 82.1 to 85.2 percent (pure-coal basis).

Swelling of the bright coals was observed to be less than that of many of the bright coals of higher carbon content.¹⁴ The percentage increase in volume showed a rough

¹³ Lessing, R., *J. Soc. Chem. Ind.*, **31**, 465-8, 671 (1912).

¹⁴ Mott, R. A., *ibid.*, **46**, 85-92T (1927); *Fuel*, **6**, 227-31 (1927).

¹⁵ Rose, H. J., *Fuel*, **5**, 57-64 (1926).

¹⁶ Mott, R. A., and Shimmura, T., *Fuel*, **7**, 472-86 (1928); *J. Fuel Soc. (Japan)*, **8**, 172-90 (1929).

correlation with increase in carbon content. Both "brights" and "hards" produced porous-structure cokes at the 1° C per minute heating rate. Similar tests carried out at a 5° C per minute heating rate gave cokes more distorted in shape. One from the coal of highest carbon content (85.2 percent) showed only partial fusion; and 4 from the coals of lowest carbon contents (82.1 to 83.7 percent), no fusion. Later experiments proved that coals with a carbon content of 85 percent or more fused only partly at the 5° C per minute heating rate.

The cokes made from the "hards" at the rapid rate of heating behaved in the same way as those made at the slow rate. The percentage alteration in volume at the rapid rate showed no general relationship between the percentage increase in volume and the carbon content. However, the 2 coals that gave lower increases in volume during coke formation at the slow rate of heating than were to be expected from their relative carbon content, compared to that of other coals in the bright series, showed the greatest relative increases in volume at the rapid rate of heating.

Damm⁸ observed the beginning of fusion by means of a stereomicroscope. A compressed sample of coal was heated gradually in a tube through which a slow stream of carbon dioxide was passed to remove the gaseous products of decomposition; the temperature was determined by a thermocouple. In many coals, visual observation of the beginning of fusion could be made very distinctly; in others, the fusion was obscured by the previous formation of tar vapors.

Berl and Schildwächter¹⁷ used a small electric tube furnace; the tube was illuminated by a small arc light. An inert at-

mosphere of hydrogen, nitrogen, or carbon dioxide was maintained in the furnace during the destructive distillation of the coal. Temperatures of (a) initial decomposition, (b) tar evolution, (c) end of coke formation, and (d) end of gas formation were observed at 45-diameter magnification by means of an Endell heating-stage microscope. For the (a), (b), (c), and (d) temperatures, respectively, in nitrogen gas, a gas flame coal showed 270, 320, 490, and 550° C; extracted gas flame coal, 200, 310, "little change," and 550° C; gas flame coal and the entire bitumen, 160, 220, 400, and 520° C; gas flame coal and solid bitumen, 160, 240, 400, and 480° C; and gas flame coal and oily bitumen, 160, 230, 390, and 500° C.

Ball and Curtis¹⁸ attempted direct observations of the softening point of single pieces of coal in a microfusion apparatus mounted on a microscope stage. No real fusion could be observed.

They devised a second apparatus in which the coal particle was mounted at the center of a horizontal steel tube and heated at a rate of not over 1° C per minute while bathed by a slow stream of pure dry nitrogen. With very fusible coals, the particle became somewhat rounded and swollen with many wide cracks over the surface, but no real fusion could be observed. The distortion temperatures found by this method checked the softening temperatures obtained by the gas-flow method for some coals, whereas for others the distortion temperatures were as much as 15° C lower than the softening temperatures.

Kattwinkel¹⁹ used powdered-coal or briquetted-coal cylinders in a transparent

¹⁸ Ball, A. M., and Curtis, H. A., *Ind. Eng. Chem.*, **22**, 137-40 (1930).

¹⁹ Kattwinkel, R., *Brennstoff-Chem.*, **11**, 329-30 (1930).

¹⁷ Berl, E., and Schildwächter, H., *Brennstoff-Chem.*, **8**, 159-60 (1928).

quartz tube fitted with a ground-in stopper and gas-outlet tube. The charged tube was placed centrally in a short, upright, thick-walled aluminum cylinder, which had a wedge-shaped slit closed by a mica window for observation of the heating process by means of a microscope lamp. The assembly was heated with a microburner, fairly rapidly to 250° C, then at 5° C per minute. A thermometer with bulb at the same height as the coal sample measured the temperature in the aluminum cylinder. Volatilization of the bitumens accompanied by expulsion of hygroscopic water ("bitumen decomposition point") was indicated by the temperature at which oils condensed on the stopper and in the gas-outlet tube. The softening point was indicated by the start of swelling, and the solidification point by the end of swelling. This temperature interval was designated the "softening zone." The stopper and gas-outlet tube were removed from the tube, an iron mantle placed around the aluminum block to provide heat insulation, and the temperature held at 520° C for 10 minutes. The quartz tube was then removed from the furnace and the volume and weight yields of semicoke determined. Yields were within 1 to 2 percent of those obtained by the Fischer assay test. Five caking and six noncaking coals were tested. The caking coals showed considerable plasticity, that is, a large difference between the temperatures of softening and solidification, and considerable increase in volume. The noncaking coals were nonswelling and nonmelting and showed no increase (some showed a decrease) in volume; with these coals only the bitumen decomposition point was recognized.

Kattwinkel later²⁰ improved the apparatus and test procedure in several re-

spects. To prevent oxidation of the 1-gram coal pellet, and to remove distillation gases more rapidly, the coal tube was provided with both gas-inlet and gas-outlet tubes through which a slow stream of carbon dioxide was passed during the test. As soon as the hygroscopic water had been driven off, a filter was placed in the gas-outlet to adsorb condensable oils and tar. The rate of heating up to 200° C was at 20° C per minute, from 200 to 300° C at 10° C per minute, and above 300° C at 5° C per minute.

With the 5 caking coals four characteristic temperature points, which indicated changing conditions and characterized the softening zone, could be established. The *bitumen decomposition point Z* was defined as the temperature at which the first distillation products in the form of light-yellow oil were adsorbed on the filter. At the *softening point E* the cleavage products (primary tar) were brown to black. This point agreed well with the softening point determined by a penetrometer test. With further temperature rise the tar formation subsided. The temperature at which the coal began to swell was designated the *swelling point B (Blähpunkt)*. Above this temperature the volatile constituents consisted only of gases. Transition of the plastic coal into the solid state took place at a still higher temperature, the *resolidification point W*, at which swelling was complete and the melted coal had solidified. This solidification point was easily and clearly established. The determination under like test conditions could be repeated with only a 2 to 3° C difference at all four fixed points. The volume increase of the coal pellet gave a measure for the degree of swelling of the coal, which was expressed in percentage of the original volume of the coal pellet.

²⁰ Kattwinkel, R., *Glückauf*, 68, 518-22 (1932).

Noncaking coals and caking coals that had lost their coking power through oxidation showed no swelling by this method of determination. With such coals the softening zone was defined by the decomposition point and a fixed point, which was taken at 75° C above the softening point and was subdivided by an intermediate point lying 50° C above the softening point.

Additional information on the 7 coals tested was obtained from quantitative determinations of the weight yields of volatile products given off between certain characteristic temperature limits. The division of volatile products from 4 fat coals and a gas coal was made as follows: below decomposition point *Z* in the preheating or predegasification zone; from *Z* to softening point *E*, first segment of the softening zone; from *E* to swelling point *B*, second segment of the softening zone; from *B* to the resolidification point *W*, third segment of the softening zone; from *W* to semicoke point *H* taken as 520° C, semicoke zone or a part of the after-degasification zone; and from *H* to coke point *K*, coking zone or the rest of the after-degasification zone. For the gas coal after some oxidation and a low-rank young coal, *E* + 50° C was used for *B* and *E* + 75° C for *W*. To obtain the amount of gas from *H* to *K* the pellet was removed, finely ground, and coked in a platinum crucible according to the Bochum crucible test at 900° C.

The evolution of gases was strongest in the caking coals in the second segment of the softening zone, that is, from *E* to *B*. The rate decreased rapidly thereafter through the third segment of softening zone *B* to *W*, and then remained the same or rose slightly in semicoke zone *W* to *H*. The oxidized gas coal gave more gas in the earlier than in the later stages. In the low-rank, noncaking coal evolution of gases

was greatest in the predegasification zone, that is, up to *Z*.

The method of Kattwinkel²⁰ was used by van Ahlen²¹ to determine the temperatures of decomposition and softening on 5 sieved sizes, ranging from less than 0.088 up to 0.75 millimeter, of raw and floated coal sludges. The lowest decomposition and softening temperatures for the raw coal sludges were obtained on the 0.50 to 0.20 millimeter size, and for the floated coal sludges on the 0.20 to 0.102 millimeter size. Correlations of the ratio of dull coal to bright coal and of fusain content for each size with its decomposition and softening temperatures were unsatisfactory. Petrographic constituents were separated by sieve analysis, which Stach²² has stated does not give quantitative results.

Pieters and Koopmans²³ heated 3 grams of coal in a rotating, horizontal, glass tube through which was passed a stream of carbon dioxide. The desired temperature, attained in 45 minutes, was then held constant for 30 minutes, until no more tar fog developed. Primary tar, determined by collecting and weighing, agreed well with results obtained by the Fischer low-temperature assay method. The cooled reaction residue product was mixed with molten resin and again cooled and hardened; the surface was ground, polished, and studied microscopically with vertical illumination. Results on coals of different rank, their petrographic constituents, and oxidized coals were illustrated by photomicrographs.

Gieseler²⁴ investigated the coking process of several coals by means of an improved Leitz heating-stage microscope.

²¹ Van Ahlen, A., *Glückauf*, **71**, 68-70 (1935).

²² Stach, E., *Lehrbuch der Kohlenpetrographie*, Gebrüder Borntraeger, Berlin, 1935, p. 249.

²³ Pieters, H. A. J., and Koopmans, H., *Het Gas*, **52**, 478-82 (1932); *Fuel*, **11**, 447-51 (1932).

²⁴ Gieseler, K., *Glückauf*, **69**, 604-7 (1933).

The first decomposition of an Upper Silesian vitrain occurred at about 350° C; its softening, between 380 and 450° C. The durain softened only partially, while the fusain was unchanged. Generally, the fat coals fused appreciably, whereas gas-rich Upper Silesian coal of high durain content melted only a little. *Esskohl* (forging coal) showed resolidification after a very short "melting" range.

Potonié and Bosenick²⁵ determined the melting points and courses of degasification of the structural constituents, *Vitrit*, *Clarit*, *Durit*, and *Fusit*, in Bismarck Seam coal by means of the heating microscope constructed the previous year by Potonié and Stockfisch. It was possible by this arrangement to examine the physical and chemical properties of the distillation products obtained at the different temperatures. Results on powdered samples were compared with similar observations on solid pieces of coal embedded in dental cement. The object of the tests on the solid coal was to make observations under such conditions that the specimen was not moved by the action of heat, as frequently happened with powdered coal. These solid samples showed, for *Vitrit*, a predegasification at about 400° C, combined with the formation of large bubbles and a main degasification at about 600° C, and formation of silver-white coke; for *Clarit*, the same properties but at higher temperatures; for *Durit*, a strong predegasification at 480° C and very many small bubbles, after-degasification at about 640° C, and dark dense coke; and for *Fusit*, no change, only a weak gas formation at 700° C.

Thiessen and Sprunk²⁶ studied micro-

scopically the effect of heat on coal. Bright coal from the Alma Seam, West Virginia, consisting of 38 percent anthraxylon, 48 percent translucent attritus, 6 percent opaque attritus, and 8 percent of fusain by area, was used in most of the work. The coal was cut into 1-inch cubes and heated in duplicate in a nitrogen atmosphere in a small electric furnace. Tests were made in successive stages at 5° C intervals from 100 to 400° C. Heating to the desired temperature was carried out at a rate of approximately 5° C per minute and was then held within 5° C of the desired temperature for 2.5 hours—long enough to allow the reactions to complete themselves.

A number of thin sections were then prepared from each of the samples and examined microscopically at various magnifications. Two types of changes were noted: (1) the formation of numerous dark-bordered cracks in the coal, and (2) the formation of vacuoles and their further development into a spongy mass. It was found that the greatest swelling occurred perpendicularly to the bedding plane of the coal and was very irregular. The point at which various constituents in the coal began to melt could be determined closely and precisely. The remaining coal was unaffected by the melting and by effervescence or sponge formation and was shown to be composed of a variety of constituents. The original paper should be consulted for further details.

Kaatz and Richter²⁷ attempted direct macro observations of the melting and re-agglomeration of coal contained in a glass tube which was heated in a salt bath. Only slight recognizable distinctions between coals were noted. Check values were hard

²⁵ Potonié, R., and Bosenick, G., *Mitt. Lab. preuss. geol. Landesanstalt*, 1933, No. 19, 75–110, esp. 82–7.

²⁶ Thiessen, R., and Sprunk, G. C., *Fuel*, 13, 116–25 (1934).

²⁷ Kaatz, L., and Richter, H. E., *Gas- u. Wasserfach*, 78, 221–9 (1935).

to obtain. Only qualitative differences were shown to exist, even in samples of the same origin, so that a comparative estimate could not be made of delivered coals.

TEST METHODS USING ABSORPTION OF COLD PYRIDINE

Hofmann and Damm²⁸ observed that with sufficiently prolonged extraction of lump coal with cold pyridine almost as much material was extracted as with hot pyridine. Marked swelling took place with certain types of coal by cold pyridine treatment.

Meyer²⁹ half-immersed blocks of coal in cold pyridine in a weighing vessel and measured the absorption and extraction with time. After 18 hours of treatment, strong swelling was observed in many samples. In general, the degree of swelling decreased with increasing rank of coal. The suitability of a given coal for coking could be predicted only to a limited extent from its swelling property in cold pyridine. Low-rank coals, such as Saxon brown coal, showed pronounced swelling at first, then shrank rapidly, whereas fat coals of better coking properties showed less rapid swelling at first and little or no aftershrinkage.

Damm³ found that the swelling shown by 6 German coals after standing for 14 days in cold pyridine was related to the expansion pressure of the coal. The degree of swelling was observed to be more marked the smaller the expansion pressure of the coal.

Chorazy³⁰ measured the gain in weight of coal samples over pure pyridine in a desiccator. Daily readings showed that old

coals, those with carbon-to-hydrogen ratios above 20 to 1, took up insignificant amounts, whereas young coals absorbed large quantities. No strict relationship was found between volatile matter content and the amount of absorption, although vitrain showed a fairly regular decrease of absorption with decrease in volatile content. In older coals, vitrain, durain, and fusain showed no differences in absorption of pyridine, but in younger coals the ability to absorb was characteristic of the petrographic composition of the coals. Vitrain absorbed the most pyridine, and fusain the least. Only vitrain gave absorptions from which the coal deposits could be characterized. Preheating at various temperatures up to 500° C caused some coals to absorb more pyridine than did the original coal. The phenomenon of plasticity occurred at temperatures similar to those that enhanced pyridine vapor absorption. Claims were made that studies of pyridine vapor absorption curves can serve for an accurate determination of the plastic state and of the state in which the coal colloid gradually passes into semiliquid gel.

Agde and Hubertus³¹ measured the penetration of pyridine into the coal sample by means of the swelling meter devised by Enslin for Freundlich and coworkers.³² Gas flame coals swelled rapidly at first and then more slowly for several days, and to a greater extent than fat coals, whose swelling was usually complete in one day. The lean coals showed intermediate swellings. The mechanism of swelling in pyridine was discussed in detail.

²⁸ Hofmann, F., and Damm, P., *Brennstoff-Chem.*, **3**, 73-9, 81-91 (1922).

²⁹ Meyer, E., *Braunkohlenarch.*, No. 18, pp. 1-58 (1927).

³⁰ Chorazy, M., *Przemysł Chem.*, **15**, 233-52, 257-70 (1931).

³¹ Agde, G., and Hubertus, R., *Braunkohlenarch.*, No. 46, pp. 1-30 (1936); *Fuel*, **16**, 288-303, 337-43, 366-75 (1937).

³² Enslin, O., *Chem. Fabrik*, **6**, 147-8 (1933). Freundlich, H., Schmidt, O., and Lindau, G., *Kolloid-Beihfte*, **36**, 43-81 (1932).

AGGLUTINATING AND FREE SWELLING
(BLÄHEN) TEST METHODS, COAL
UNDER NO ADDED LOAD

Numerous crucible and tube tests for the determination of "caking index," "caking power," or "agglutinating index" have been described. Two types of test methods, differing somewhat in procedure and recognized as suitable, have been employed. In one, the coal sample is mixed with some inert material, such as sand, electrode carbon, or silicon carbide; in the other, the coal alone is carbonized. The agglutinating test involves the capacity of the coal to cohere large proportions of some inert material. A distinctive feature of this test is that the original charge of coal and inert material seldom swells during the test.

AGGLUTINATING-VALUE TEST METHODS

The agglutinating-value test is a small-scale laboratory test method that gives an approximate measure of the quantity and quality of the material in coal that fuses and becomes plastic on heating in the absence or near absence of air. This property of caking or agglutination is necessary for coals used for coke manufacture, but when coals are burned on grates it often causes trouble due to obstruction of air through the fuel bed.

It was first shown by Richters in 1870³³ that those coals known to produce the best commercial cokes were capable of incorporating a higher admixture of inert material to give a carbonized residue of definite crushing strength than were the more inferior coking coals. Richters carbonized, at approximately 950° C until the visible flame disappeared, mixtures of air-dried, finely powdered coal and washed, powdered

quartz in a platinum crucible. One gram of coal and increasing amounts of quartz were carbonized until the resulting button just sustained a 500-gram weight, without crumbling. The caking or agglutinating index was expressed as the ratio of quartz to coal in the mixture of limiting crumbling strength. Numerous modifications of this test have been made by investigators employing different inert materials and variations in both apparatus and test procedure.

In 1929, Marshall and Bird³⁴ summarized and reviewed critically the more important test methods proposed by earlier investigators.^{33, 35} All these methods, ex-

³⁴ Marshall, S. M., and Bird, B. M., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 340-88 (1930).

³⁵ (a) Campredon, L., *Compt. rend.*, **121**, 820-2 (1895); *Rev. chim. ind.*, **7**, 8-9 (1896). (b) Strahan, A., and Pollard, W., *Mem. Geol. Survey Engl. Scot. Wales*, 1908, 91 pp. (c) Lessing, R., *J. Soc. Chem. Ind.*, **31**, 465-8, 671 (1912); *Fuel*, **2**, 152-5, 186-90 (1923); Chester, C. H., *Gas J.*, **164**, 517-22 (1923); *Gas World*, **79**, 472-6 (1923). (d) Dunn, J. T., *J. Soc. Chem. Ind.*, **32**, 397-8 (1913); *Gas World*, **58**, 770 (1913). (e) Meurice, A. A., *Ann. mines Belg.*, **19**, 625 (1914); *Colliery Guardian*, **117**, 1559-60 (1919); *Chaleur et ind.*, **4**, 45-52 (July, 1923); *Fuel*, **2**, 305-8 (1923); Sainte-Claire Deville, J., *Fuel*, **2**, 296-7, 345-9 (1923). (f) Charpy, G., and Godchot, M., *Compt. rend.*, **164**, 906-8 (1917). (g) Sinnatt, F. S., and Grounds, A., *Trans. J. Soc. Chem. Ind.*, **39**, 83-6T (1920). (h) Weighell, A., *J. Soc. Chem. Ind.*, **41**, 17T (1922). (i) Bone, W. A., Pearson, A. R., Sinkinson, E., and Stockings, W. E., *Proc. Roy. Soc. (London)*, **A100**, 582-98, esp. 595 (1922); Wheeler, R. V., *Fuel*, **1**, 61 (1922). (j) Gray, T., *Fuel*, **2**, 42-5 (1923); *Dept. Sci. Ind. Research (Brit.) Fuel Research Survey Paper 2* (1923), 28 pp., esp. 10-1; *Fuel*, **3**, 27-30, 53-6, 93-7, 140-2, esp. 95-7 (1924); *Dept. Sci. Ind. Research (Brit.) Research Survey Paper 7* (1927), 35 pp., esp. 10-1. (k) Badarau, A., and Tidswell, F. V., *Fuel*, **2**, 61-6 (1923); Burdekin, J. T., *Dept. Sci. Ind. Research (Brit.) Fuel Research Survey Paper 8* (1927), 21 pp.; Anon., *Gas J.*, **178**, 29 (1927). (l) Ahrens, B., *Brennstoff-Chem.*, **5**, 268-70 (1924); Kreulen, D. J. W., *Brennstoff-Chem.*, **5**, 381-3 (1924). (m) Qvarfort, S., *Fuel*, **4**, 154-60 (1925). (n) Marson, C. B., and Cobb, J. W., *Gas J.*, **171**, 39-43 (1925). (o) Barash, M., *Gas J.*, **172**, 17-27, Coke Competition Number

³³ Richters, E., *Dinglers Polytech. J.*, **195**, 71-3 (1870).

cept those by Lessing, Charpy and Godchot, Qvarfort, and Coffman and Layng, used some form of inert material with the coal. A summary of these early test methods that used a mixture of an inert material and coal shows the wide diversity of various factors which affect an empirical, although sensitive, test of this kind:

1. Most of the test methods using an inert material (quartz, sand of rounded- or sharp-edged grains, anthracite, coke, ash-forming constituents, or electrode carbon) specified that it be closely sized and in some instances receive other purifying treatment.

2. The size of coal ranged from minus 30- to plus 120-mesh; three tests even used sized coal. Specifications for moisture content of the coal, if given, ranged from saturation to coal dried at 105° C.

3. Great diversity of opinion was shown in regard to the best method of preparing the coke buttons. Some tests changed both the weight and volume of the buttons before coking; this group included all tests in which different weights of inert material were added to a constant weight of coal. In other tests only the volume was changed; this group included tests using a constant weight of button but different proportions of coal and inert material. Only three tests maintained both volume and weight constant. Adequate precautions for preventing segregation of the inert material and the coal in the interval between mixing and carbonization, if observed, were not recorded. Only one test method recognized the necessity of compressing the mixed sample to bring the components of the buttons into intimate contact before carbonizing. Crucibles and cylindrical tubes of different shapes and materials were used as containers for the buttons. Different end temperatures

and rates of heating with various types of burners and electric furnaces were employed.

4. Those tests on buttons containing different proportions of inert material involved some fixed procedure such as supporting a given weight, sometimes with the determination of the percentage of detritus; several tests depended on visual examination or some other scheme, involving the skill and judgment of the individual operator, such as breaking the button in the fingers. Buttons with constant proportions of coal and inert material were generally crushed in a testing machine. Only three tests involved trimming-up of the surface of the buttons prior to crushing.

5. The favorite method of reporting the agglutinating value was the maximum ratio by weight of inert material to coal in the button that just met or failed to meet the breaking test of the given test. In some tests this had only a single value, the maximum attained; in others, the results were shown as a curve in which the breaking strength was plotted against the ratio of inert material to coal. In a few instances, an equation that incorporated the inert material-coal ratio, breaking load, percentage of fines produced by handling and crushing, and sometimes other factors into a single number was used. This number bore no direct relationship to the load sustained by the button. In several tests, the crushing strength per unit area was taken as the agglutinating value.

Marshall and Bird concluded from their examination of the work of these earlier investigators that the agglutinating test was sound in principle but that the procedures of the various proposed test methods were faulty. Essentially the same conclusions were reached at about the same time by other workers³⁸ who studied criti-

(Nov. 9, 1925); *Fuel*, **6**, 532-51 (1927); *Trans. J. Soc. Chem. Ind.*, **45**, 151-77T (1926); *Gas J.*, **173**, 276-80 (1926); Dann, H., *Gas J.*, **173**, 477-8 (1926); Fulweiler, W. H., and Cleveland, T. K., *Proc. Am. Gas Assoc.*, **1927**, 1399-410. (p) Kattwinkel, R., *Gas- u. Wasserfach*, **69**, 145-50 (1926); *Glückauf*, **62**, 972-3 (1926); *Fuel*, **5**, 347-55, 431, 980-1 (1926); *Brennstoff-Chem.*, **11**, 329-30 (1930); Bähr, H., *Fuel*, **5**, 430-1, 978-80 (1926). (q) Coffman, A. W., and Layng, T. E., *Ind. Eng. Chem.*, **20**, 165-70 (1928).

³⁸ Slater, L., *Dept. Sci. Ind. Research (Brit.)*, *Fuel Research Board Rept.* **1928-9**, 110-9. De Vos, G., *Natuurw. Tijdschr.*, **12**, 163-70 (1930). Leeuw, J. de, and Brender à Brandis, G. A., *Het Gas*, **50**, 143-4 (1930). Pieters, H. A. J., and Smeets, G., *ibid.*, **51**, 228-34 (1931), **52**, 153-5 (1932). Crussard, L., and Gauzelin, M., *Rev. ind. minérale*, **12**, No. 283, 389-408, No. 284, 409-26 (1932); *J. usines gaz.*, **57**, 33-41, 65-70, 82-9, 136-44 (1933).

cally certain of the earlier published agglutinating test methods.

The method developed by Marshall and Bird³⁴ consisted in mixing 22.725 grams of 40- to 50-mesh Tyler sieve Ottawa sand with 0.07 gram of glycerol and 2.275 grams of minus 100-mesh (Tyler sieve) coal. Ten such mixtures were prepared and carbonized for 20 minutes at a maximum temperature of 950° C. When the buttons were to be broken the loose material was poured off and the crucible turned over so that each button was inverted on a soft rubber pad. The top of the button was likewise protected by a small rubber pad. The button, with pads in position, was placed in the center of the platen of the testing machine, and crushed. Record was made of the maximum crushing strength in grams and of any unusual feature of the test. If any button differed in crushing strength from the average of the 10 buttons by more than 10 percent the test was repeated.

The agglutinating values of 18 coals of various ranks from different parts of the United States increased with increasing relative strength of known cokes manufactured from them. Very definite increases were noted in the agglutinating values with increases in the 2-inch shatter tests of the cokes from 5 of these coals. Correlations between the agglutinating values and certain constituents of the coals showed general trends. The agglutinating values *decreased* with increase in the oxygen content of the coals and with increase in the carbon monoxide and carbon dioxide content of their distillation gases, but they *increased* with the carbon-oxygen and hydrogen-oxygen ratios of the coals. The plotted points for all these correlations were scattered somewhat, probably owing to influences that affected the agglutinating

values without affecting to the same degree the other properties just cited.

Johnson and Yancey³⁷ studied various factors affecting the method of test as proposed by Marshall and Bird. The factors studied in relationship to the agglutinating values obtained included: (1) the temperature of carbonization; (2) the time of carbonization; (3) the ratio of sand to coal; (4) the effect of using sponge-rubber capings of different thickness in the machine for determining the breaking strength of the buttons; (5) the amount and nature of the liquid added to the coal-sand mixture to prevent segregation; and (6) a comparison of the agglutinating values obtained from samples of the same coal by three different workers.

Tests on 5 coking coals, determined at 100° C intervals from 650 to 1,050° C, showed, except for 1 Utah coal whose agglutinating value continued to decrease, that the agglutinating values decreased with increase in the temperature of carbonization up to about 950° C and then increased slightly at 1,050° C. The carbonizing temperature of 950° C, advocated by Marshall and Bird, which gave the minimum agglutinating value under the test conditions used, was considered most satisfactory.

The effect of time of carbonization on the agglutinating values of 2 Washington coals was studied for time intervals of 7 to 120 minutes. The agglutinating value decreased sharply up to 10 and 18 minutes of heating for the two coals. This was attributed to a decrease in the temperature of the furnace caused by insertion of the cold sand-coal samples. Beyond the 20-minute period the slope of the curve, that is, agglutinating values, in grams,

³⁷ Johnson, K. A., and Yancey, H. F., *U. S. Bur. Mines, Repts. Investigations* **3011** (1930), 7 pp.; *Fuel*, **9**, 517-21 (1930).

plotted against time of carbonization, in minutes, was much less pronounced. The 20-minute period, recommended by Marshall and Bird, was adopted as satisfactory for carbonization.

The effect of changing the ratio of sand to coal by steps from 2 : 1 to 20 : 1 with carbonization for 20 minutes at 950° C was to decrease the agglutinating values as the ratio of sand to coal was increased. Mixtures of 10 parts of sand to 1 part of coal by weight, recommended by Marshall and Bird, were considered satisfactory for the usual range of agglutinating values obtained with coking coals.

Tests on rubber-sponge cappings between the buttons and the platens of the machine used for determining the breaking strength of the buttons suggested that rubber sponges $\frac{3}{16}$ inch thick and of density about 0.38 be used until a more satisfactory capping could be found.

The crushing strength of the buttons was found to decrease with increased amounts of added glycerol or water. Segregation of the sand and coal was found to be prevented best by adding 1 drop of glycerol from a surface-tension dropper of the Traube type.

Comparative agglutinating values obtained on the same 3 coals by three different workers in different laboratories using the Marshall-Bird procedure, except that the coal samples were first air-dried under laboratory conditions instead of at 105° C, before being crushed to 100-mesh, gave fairly satisfactory check results.

Davis and Pohle³³ studied the effect of the addition of various finely ground mineral inerts as a part of the coal sample on the agglutinating value of Pittsburgh Seam

(Banning No. 1 mine) coal. The strength of the coke buttons increased up to about 25 percent additions of the weight of the coal. The effect varied somewhat with the nature of the inert material, but invariably a definite increase was found. Results were similar to those obtained by Dunn,³⁹ who studied the effect of natural ash-forming materials in coal. Buttons made from the coal-mineral inerts and electrode carbon instead of sand decreased regularly in strength with increasing amounts of the added mineral inert, but with fusain this decrease was only slight up to additions of 20 percent. The action between inert and coal was physical, rather than chemical. The effect of the fineness of the added inert, if mineral, was specific; if entirely carbonaceous, no specific effect was observed.

The many variables affecting the agglutinating-value test method were studied by Selvig, Beattie, and Clelland⁴⁰ with a view of standardizing the test. On the basis of this investigation a number of major changes in both apparatus and test procedure were incorporated in a "proposed method of test for agglutinating value of coal."⁴¹ Specifications for the apparatus and the recommended test procedure were almost identical with those of the new improved method proposed⁴² using silicon carbide instead of sand as the inert material in the agglutinating mixture.

³⁹ Dunn, J. T., *J. Soc. Chem. Ind.*, **32**, 397-8 (1913); *Gas World*, **58**, 770 (1913).

⁴⁰ Selvig, W. A., Beattie, B. B., and Clelland, J. B., *Proc. Am. Soc. Testing Materials*, 1933, preprint, 17 pp.; *Proc. Am. Soc. Testing Materials*, **33**, Pt. II, 741-60 (1933); *Mining Met. Investigations, U. S. Bur. Mines, Carnegie Inst. Tech., Mining Met. Advisory Boards Coop. Bull.* **60** (1933), 17 pp.

⁴¹ *Proc. Am. Soc. Testing Materials*, **34**, Pt. I, 457-62 (1934).

⁴² *ASTM Standards on Coal and Coke*, Am. Soc. Testing Materials, Philadelphia, 1938, pp. 95-100.

³³ Davis, J. D., and Pohle, W. D., *Ind. Eng. Chem.*, **23**, 1427-31 (1931); *Mining Met. Investigations, U. S. Bur. Mines, Carnegie Inst. Tech., Mining Met. Advisory Boards Coop. Bull.* **55** (1932), 10 pp.

Experience in the U. S. Bureau of Mines and other laboratories showed that different shipments of Ottawa sand, used as the standard inert material, varied in physical structure. Sand having a relatively large amount of grains with frosted surfaces gave higher agglutinating values than sand with more glossy surfaces. Tests on different lots of silicon carbide showed that this material was sufficiently uniform for use as the inert material. Cooperative tests with another laboratory showed good agreement when the same coals were tested and different lots of silicon carbide were used. The commercial availability of silicon carbide (Carborundum) of uniform grain structure and the excellent results obtained with it led to its substitution for sand as the specified inert material.

The *British standard method* for the determination of the agglutinating value of coal⁴³ is a modified Gray-Campredon test. The test is empirical and is claimed to show good reproducibility by one individual operator, but a high degree of concordance is not to be expected between different operators. It is therefore recommended that the agglutinating value as determined by the test should be applied to assessing the agglutinating index of the coal according to a specified grouping.

Applications of the Agglutinating-Value Test. There is lack of agreement among coal chemists as to the value of this test to evaluate coals for coke-making. It is probably too much to expect close correlation with the strength of commercial cokes. The test has been shown to be of value in detecting deterioration of coking properties of coal due to storage. Marshall, Yancey, and Richardson,⁴⁴ from

studies on 3 coals that had been exposed to oxidation in air for various periods of time, concluded *tentatively* that the rate of loss in agglutinating power (Marshall-Bird method) followed closely the rate of increase in the oxygen content of the coal. Rose and Sebastian,⁴⁵ on the contrary, concluded that there appeared to be no correlation between the agglutinating values and the oxygen content of coals, after controlled oxidation at 80° C for various periods of time.

Barkley and Burdick⁴⁶ determined the agglutinating value of 25 coals by the proposed A.S.T.M. method⁴¹ using sand as the inert material, but employing sand-coal ratios of 10 to 1, 14 to 1, 18 to 1, and 22 to 1. The values obtained at the 18 to 1 ratio gave the best correlation with the caking action of the same coals determined in various types of natural-draft and forced-draft burning equipment. Only correlations of a qualitative nature could be considered, because the observations of the nature of the coke mat and the rapidity of coking must necessarily be described in general terms.

Fish⁴⁷ also used this proposed A.S.T.M. (sand) method for determining the agglutinating values of 9 low-volatile Virginia coals. Two of the coals had been classed as bituminous, and 7 were generally regarded as semianthracites. Six of the semianthracites showed zero agglutinating values at all four standard sand-coal ratios. One so-called semianthracite, Groselose Seam coal, although possessing certain properties of a semianthracite when handled and burned, contained more volatile matter and an even lower fuel ratio than

⁴³ *British Standards Institution, Pub. Dept.*, 705 (1936), 9 pp.

⁴⁴ Marshall, S. M., Yancey, H. F., and Richardson, A. C., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 389-93 (1930).

⁴⁵ Rose, H. J., and Sebastian, J. J. S., *ibid.*, 88, 556-84 (1930); *Fuel*, 11, 284-97 (1932).

⁴⁶ Barkley, J. F., and Burdick, L. E., *Power Plant Eng.*, 3S, 132-4 (March, 1934).

⁴⁷ Fish, F. H., *Virginia Polytech. Inst., Eng. Expt. Sta. Series Bull.* 20 (1935), 14 pp.

the 2 bituminous coals. It showed much lower agglutinating values than those of the 2 bituminous coals at all sand-coal ratios. The agglutinating-value test was suggested as a means of classifying coals, particularly those on the borderline between groups that might be improperly classified according to other properties.

In summary here, it may be said that agglutinating-value tests are helpful in the selection of coals for various uses, provided that the agglutinating values or indexes are correlated with the peculiar characteristics of the coals best suited for these uses. The test appears to be somewhat limited for the so-called scientific classification of certain coals. The method is not as applicable to weakly agglutinating coals as to those coals that contain enough agglutinating material to produce buttons that will not pulverize under a minimum weight (say, 500 grams) at a ratio of sand to coal of 15 to 1. Lower sand-to-coal ratios do not give homogeneous buttons. For coal-classification purposes, the method determines which coals are definitely caking rather than which are nonagglutinating in the sense that they contain no agglutinating or agglomerating material whatever. The method is limited, therefore, for distinguishing between positive and negative caking.

LABORATORY CRUCIBLE AND TUBE COKING TESTS ON COAL ALONE

Slater⁴⁸ studied the relation between swelling power and coking at different rates of heating. A 20-gram sample of through 60-mesh coal was held in semicylindrical form by means of loose asbestos stoppers in the middle 6-inch length of a fused-silica tube which was placed horizontally in a carefully regulated electric tube (Gray-

King assay) furnace,⁴⁹ preheated to 300° C. Three series of tests were carried out in which the times of heating were 1, 3, and 4.5 hours, respectively, from the time of insertion of the tube in the preheated furnace to a final temperature of 600° C, which temperature was then maintained for another hour. Photographs of the cokes obtained showed that swelling was materially affected by the rate of heating. The slowest rate gave the most distinct differences among the 10 coals tested. The degree of swelling was defined as the ratio of coke volume to the original coal volume. Bradley and Mott⁵⁰ used Slater's method but pointed out that no simple numerical measure of the cross-sectional swelling can be given since the coal column was not free to swell along its length.

Mott¹⁴ coked freshly crushed sized coal in covered, clamped cast-iron capsules. The coals tested and the heating conditions were the same as those described previously (see page 170). The anthracite coal yielded a noncoherent residue. The 5 bright, good coking coals (85.2 to 88.4 percent carbon on the dry, ash-free, sulfur-free basis) gave well-fused, glistening residues. The 2 bright inferior coking coals (82.4 and 84.4 percent carbon) yielded strong residues in which the individual coal particles had coalesced, but their shapes were still apparent. The 3 bright coals containing 81.6, 79.9, and 78.9 percent carbon, respectively, yielded weak residues with decreasing coherency in the order given. The 3 samples of "hards" (durains) with

⁴⁸ Slater, F., *Fuel*, **6**, 82-4 (1927).

⁴⁹ Gray T., and King, J. G., *Dept. Sci. Ind. Research (Brit.)*, *Fuel Research Tech. Paper 1* (1921), 13 pp.

⁵⁰ Bradley, G. W. J., and Mott, R. A., *Trans. Inst. Mining Engrs. (London)*, **76**, 200-14 (1928-9); *Colliery Guardian*, **137**, 2457-60 (1928).

carbon percentages of 88.4, 87.1, and 83.8 yielded strong residues in which the particles had coalesced, but their shapes were still evident. An almost entirely coherent residue was obtained from durain containing 83.3 percent carbon, whereas residues from durains containing 81.7 and 81.6 percent carbon were entirely noncoherent.

A study of the above results shows that the swelling and coherency of the residues decreased almost linearly with decreasing carbon content. In coke formation from crushed particles of coal, wetting phenomena would appear to have great importance. Coals that do not furnish much or suitable wetting liquids do not make strong cokes.

Mott and Shimmura¹⁶ carried out tests on moderate and inferior coking coals crushed to the same size and coked in cast-iron capsules similar to those used by Mott.¹⁴ Heating conditions, however, were different. The charged capsules were heated in an inert atmosphere at a rate of 1° C per minute to 600° C, and then the temperature was raised rapidly to 900° C. The coals tested were the same series of 9 "brights" and 5 "hards," used in the 1-inch cube tests (see page 170). For the bright coals, only the one of lowest carbon content (82.1 percent, pure-coal basis) retained the shape of the original coal particles in the coke residue; in all others, the particles had coalesced to give a more or less uniform coke residue. Four bright coals with carbon contents between 84.3 and 85.2 percent had swollen to the limit possible in the capsule, and their black, lustrous cokes apparently were strongly fused. One bright coal containing 84.3 percent carbon did not swell but produced an apparently strong coke whose color was intermediate between black and gray. Three bright coals with carbon content between 82.9 and 83.7 percent showed

less swelling than higher-carbon coals, and apparently gave strong, gray cokes. The bright coal of lowest (82.1 percent) carbon content gave no appearance of fusion. The particles were bound together without losing their shape and were gray in color. The 5 "hards" (durains) gave residues much like that of the bright coal containing 82.1 percent carbon.

Lambris⁵¹ discussed in minute detail a large number of the crucible tests and swelling tests on coal under an *applied* load. He pointed out that the results obtained by such methods usually were not comparable among themselves and never showed the maximum possible degree of swelling of a coal, because the manner of heating permitted a crust of coke to form around the noncoked portion of the coal sample and thus prevented its further expansion. Lambris determined the maximum degree of swelling of coal by placing the sample above an insulating layer of kieselguhr in a platinum crucible and heating at 900° C without a cover. A coke film quickly formed on the top of the coal and acted as an insulator but did not prevent expansion, because the coal was heated further only from the sides. The degree of swelling was found to be inversely proportional to the heat conductivity of the kieselguhr and of other materials tried. Swelling was enhanced by the use of very fine coal.

Lambris believed that under the conditions of this test maximum swelling of the coal took place, because complete enclosure of the coking mass by coke shells was prevented until all the constituents of the coal responsible for the swelling had been completely carbonized. The method was claimed to be capable of exact duplication and to permit the determination of

⁵¹ Lambris, G., *Brennstoff-Chem.*, **9**, 341-6 (1928), **10**, 44-50, 66-7 (1929).

the exact degree of swelling. No conclusions can be drawn from this measurement of swelling as to the expansive force, coke yield, or after shrinkage of the coke. In the body of his paper, Lambris explained in detail his conception of (free) swelling but unfortunately used the term "Treiben" in the sense of the term "Blähen." The careful distinction in meaning between these two terms made by Damm³ had apparently been overlooked. Lambris in a note at the end of the second part of his paper and in his reply to Damm agreed to the substitution of the word "Blähen" for "Treiben" throughout the body of his paper.

Cummings and Ivison⁵² measured the apparent volume of coke produced from 1 gram of coal heated for various times up to 7 minutes in a furnace maintained at 960° C. The maximum volume was obtained after 1.5 or 2 minutes of heating.

Test conditions in the six investigations just reviewed were widely diversified. These tests lack standardization, and the results obtained do not differentiate quantitatively between different coals. In recent years the widely used coke-button gradings made from residues left in the crucible after the standard volatile-matter determination have been of great value in classifying coals for various purposes. This test has recently been designated the "agglomerating test."

AGGLOMERATING INDEX OF COAL

The "agglomerating index" is a grading index based on the nature of the residue from a 1-gram sample of coal when heated at $950^{\circ} \pm 20^{\circ}$ C in the A.S.T.M. standard volatile-matter determination. The coke residues from various coals or blends are quite different in physical structure and

color. Beginning in 1934 with the excellent work of Gilmore, Connell, and Nicolls,⁵³ intensive studies have been made of the nature of these residues in relation to other tests for evaluating the agglutinating and agglomerating characteristics and also to the general commercial coking properties of individual coals or blends. The residue, after removal from the platinum crucible, is graded in comparison with standard buttons from coals whose characteristics are known. These authors proposed the use of the agglomerating index for indicating the dividing line between noncaking coals and those having weakly caking properties.

The agglomerating index has been adopted as a requisite physical property to differentiate semianthracite from low-volatile bituminous coal and also high-volatile C bituminous coal from subbituminous A coal.⁵⁴ All coals analyzed by the U. S. Bureau of Mines since November 15, 1934, have been classified according to agglomerating properties in accordance with Table I.

Barkley and Burdick⁵⁵ pointed out that the agglomerating index is useful in differentiating those coals that, according to their analyses, would fall into a bordering group inconsistent with their agglomerating properties. From the standpoint of the caking action of coal in coal-burning equipment the agglomerating index has some interest. For example, coals having indexes (see Table I) *N*Aa or *N*Ab, such as anthracites or semianthracites, certainly do not give any trouble from caking,

⁵³ Gilmore, R. E., Connell, G. P., and Nicolls, J. H. H., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 255-66 (1934).

⁵⁴ *Am. Soc. Testing Materials Standards*, 1939, Pt. III, 1-6 (D388-38). *Am. Standard M20.1*, 1938.

⁵⁵ Barkley, J. F., and Burdick, L. R., *U. S. Bur. Mines, Repts. Investigations* **3424** (1938), 8 pp.

⁵² Cummings, G. T., and Ivison, N. J., *Fuel*, **15**, 162-4 (1936).

TABLE I

AGGLOMERATING AND CAKING PROPERTIES OF COALS BASED UPON EXAMINATION OF RESIDUE INCIDENT TO THE VOLATILE-MATTER DETERMINATION *

Class	Designation	Group	Appearance of Residue from Standard Method for Determination of Volatile Matter in Coal
Nonagglomerating † (button shows no swelling or cell structure and will not support a 500-gram weight without pulverizing)	NA—Nonagglomerate		NAa—Noncoherent residue
			NAb—Coke button shows no swelling or cell structure and after careful removal from the crucible will pulverize under a 500-gram weight carefully lowered on button
Agglomerating † (button shows swelling or cell structure or will support a 500-gram weight without pulverizing)	A—Agglomerate (button dull black, sintered, shows no swelling or cell structure, will support a 500-gram weight without pulverizing)		Aw—Weak agglomerate (buttons come out of crucible in more than 1 piece)
			Af—Firm agglomerate (buttons come out of crucible in 1 piece)
	C—Caking (button shows swelling or cell structure)		Cp—Poor caking (button shows slight swelling with small cells; has slight gray luster)
			Cf—Fair caking (button shows medium swelling and good cell structure; has characteristic metallic luster)
			Cg—Good caking (button shows strong swelling and pronounced cell structure with numerous large cells and cavities; has characteristic metallic luster)

* Based upon ref. 53.

† Agglomerating index—coals that in the volatile-matter determination produce either an agglomerate button that will support a 500-gram weight without pulverizing or a button showing swelling or cell structure shall be considered agglomerating from the standpoint of classification.

whereas those with the *Cg* indexes include heavy caking coals. Fuel-bed observation of 26 coals, all with an index of *Cg*, were made in coal-burning equipment, including hand-fired grates and various types of stokers. The study showed that the agglomerating index does not give specific but only general or broad information on the caking action of coal in furnaces. The

method of defining the caking was that used by Barkley and Burdick in an earlier paper⁴⁶ that attempted the correlation of laboratory agglutinating values with the caking action of coal in the furnace.

Extensive experience by workers in the Canadian Bureau of Mines with the grading of coke buttons from the standard volatile-matter determination at 950° C showed

that these gradings indicate only general commercial coking properties. It was observed that the grayish, cokelike appearance of the buttons became more pronounced as swelling increased and that for the same grading the swelling of the coke button might vary considerably. Gilmore, Connell, and Nicolls⁵³ claimed, therefore, that the evaluation of a coal or blend by means of the "swelling index" determined on the coke button when carbonized at 600° C as described by Swartzman, Burrough, and Strong⁵⁴ is important and necessary as a supplement to the coke-button gradings.

With virtually all coking coals the plastic stage has been passed at about 500° C. During this stage different coals evolve varying amounts of volatile matter and show varying degrees of swelling. However, the quality of coke produced at 500° C does not show close correlation either with swelling, with quantity of volatile matter evolved, or with residual volatile matter found at this temperature. Between 500 and 600° C greater thermal decomposition of the coal takes place, and shortly above 600° C all the tar has been evolved. Hence, it was believed by Swartzman, Burrough, and Strong that 600° C is a more critical temperature with respect to resultant coke quality than any other, and that the relationship between swelling and volatile matter at 600° C should afford a reliable prediction of the quality of commercial coke to be expected from different coking coals.

To check this conclusion, the volatile matter evolved from 86 coals at 600° C, as well as at 500 and 950° C, and the volumes of the resultant coke buttons were deter-

mined. Marked variations were observed in the volume of the buttons for the same coal or blend for the three temperatures, 500, 600, and 950° C. The arrangement of coals tested at 600° C did not always differentiate sharply among the various types of coals. In some instances, two coals yielding different quantities of volatile matter gave coke buttons of equal volume. This fact indicated that the coal giving the smaller quantity of volatile matter must have greater swelling power than the coal yielding the larger quantity of volatile matter. The data were calculated, therefore, in terms of "swelling indexes." Calculation of the "swelling index" was based upon the assumption that the average volume of 1 gram of finely ground coal is 2 cubic centimeters, from which

$$\text{Percentage swelling} = \left[\frac{\text{Volume of button in cc} - 2 \text{ cc}}{2 \text{ cc}} \right] \times 100$$

and

$$\text{Swelling index} = \left[\frac{\text{Percentage swelling} + \text{Percentage volatile matter (dry basis)}}{100} \right] \times 100$$

The volatile-matter contents, dry basis, of 86 coals and blends of coals upon which byproduct coke data were available were plotted against the swelling indexes of these coals. Coals or coal blends used for the production of coke of similar quality were found to fall into groups in different sections of the diagram. Figure 4, reproduced from the paper by Swartzman, Burrough, and Strong,⁵⁴ shows thirteen sections defined by certain limits of the dry volatile-matter content and swelling index at 600° C. The portion of Section IV in Figure 4 between the swelling indexes of 650 and 900 may be considered the criti-

⁵³ Swartzman, E., Burrough, E. J., and Strong, R. A., *Can. Dept. Mines, Mines Branch*, No. 737-2 (1933), 24 pp.; *Invest. Fuels Fuel Testing*, No. 737, 36-37 (1934).

cal region for byproduct cokes. From this region the physical properties of this type of coke diverge continuously in three directions through the sections in either decreasing or increasing magnitude. The direction of the change in the physical properties of the cokes is shown by the three curved arrows radiating from Section IV. For more detailed data on the coals and

coal blends whose properties are such that byproduct cokes of the described characteristics may be expected, the original paper should be consulted.

The British Standards Institution⁵⁷ has modified the "swelling number" test devised by the Research Section of the

⁵⁷ British Standards Institution, Pub. Dept., No. 804 (1938), 17 pp.

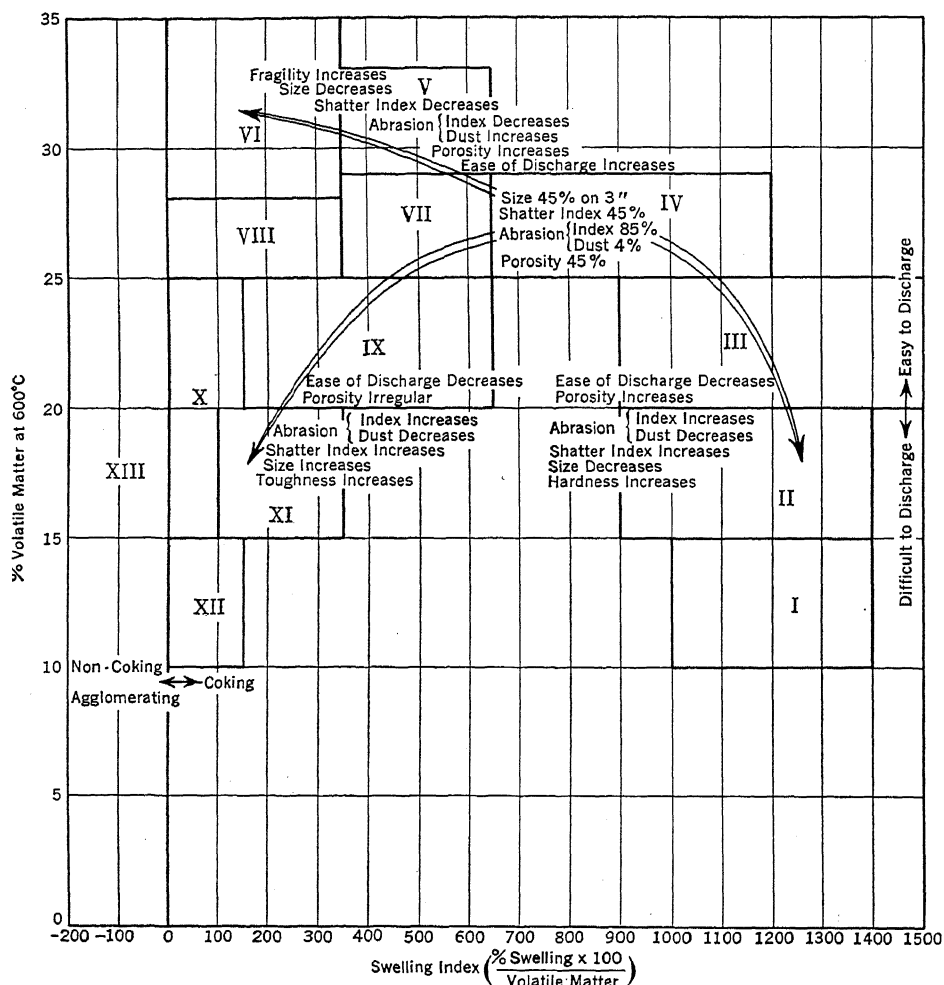


FIG. 4. Physical properties of cokes based on percent of dry volatile matter and swelling index of coals at 600° C.⁵⁸

Woodall-Duckham Companies.⁵⁸ The special value of the modified test lies in the use of a crucible of special shape, of a leveled coal surface, and of standardized unidirectional heating by means of a gas flame to produce a coke button of regular shape, which can be simply assessed by comparison with standard profile outlines. The mean value of four tests on the same coal sample is stated to be correct within ± 1 unit in 99 out of 100 cases and within ± 0.5 unit in 80 out of 100 cases.

Following these specifications, the swelling number of the button is the number of the standard profile outline that most nearly matches the largest profile of the button. Fourteen standard profile outlines of different shapes and heights, whose increasing areas are numbered from 1 to 9 in units of 0.5, permit close comparison. The mean swelling number of the four buttons, expressed to the nearest half unit, is reported. If a powder is obtained, or if the button is nonswollen (swelling number 1) and will not bear, without crumbling, a 500-gram weight, the coal is described as "nonagglomerating." If such a button merely cracks into a few firm pieces, it is called "agglomerating," as are all the swollen buttons.

The relationship between the B.S.I. crucible swelling numbers and the carbon and hydrogen contents (Parr unit coal basis) may be expressed by the equation:

$$\text{Swelling number} = 1.4 \div (H - 4.0) [(C - 94) + 11(H - 4.0)]$$

When the swelling numbers are plotted against the percentages of carbon a series of straight lines representing different hydrogen contents may be drawn in the diagram. These isohydrogen lines, if ex-

tended, would meet at a swelling number of 15 and a carbon content of 94 percent. The diagram indicates that no coal containing less than 4.0 percent hydrogen (Parr basis) will swell in the B.S.I. crucible test and that coals with less than 78 percent carbon and 5.45 percent hydrogen would give a negative swelling number, that is, they are noncaking. These indications agree with practical experience with such coals. The crucible test is claimed to be useful, especially for coals of low swelling power, such as coals containing less than 82.5 percent carbon, and high-rank coals of low hydrogen content, but may fail to distinguish the swelling power of coals with a carbon content of 87 to 91 percent. A wider range of swelling numbers than the 9 classes, each with a half unit of swelling from 5 to 9, into which the coking coals have been divided, is desirable. The rapid rate of heating causes some coals to agglomerate that would not do so in normal coke-oven operation. Any predictions from B.S.I. swelling numbers as to which coals, particularly those of lower carbon content, can be used for coke-making are of doubtful value.

LARGE-SCALE BOX AND MUFFLE TESTS

Koppers' muffle test,⁵⁹ developed about 1906, employed a sheet metal box of the same width as that of a commercial coke oven. The box was divided by a riveted partition into two unequal-size compartments. The larger chamber was charged with a given amount of coal of known bulk density. The box was placed in the oven, which was then charged in the usual manner. During coking the swelling coal pressed against the partition wall, shearing the rivets, and the expanded portion extended into the empty compartment of the

⁵⁸ Smith, E. W. Finlayson, T. C., Spiers, H. M., and Townend, F. S., *Gas J.*, **172**, 3-16 (1925) (Coke Competition No.).

⁵⁹ Koppers, H., and Jenkner, A., *Glückauf*, **67**, 353-62 (1931); *Fuel*, **10**, 232-9, 273-7

box. The differences in coking capacity of various coals could be observed clearly.

In the Otto Company clay muffle test,^{60, 61} a uniformly packed coal sample was coked in a fire-clay muffle which had been preheated to 900 to 1,000° C. The relative expansion of different coals was detected from relative bulging of the muffles; highly expanding coals caused the muffles to burst. An accurate differentiation of individual coals was not possible by this method. A coal containing different moisture contents in three tests—(a) dry, (b) 8.0 percent, and (c) 17.1 percent—showed no expansion in (b) but caused the muffles to burst in (a) and (c).

In the Waldenburg muffle test,^{61, 62} developed in 1926 by Krüger and Arenfeld, the clay crucibles used originally were shattered almost regularly by the high expansion pressures developed by many of the blends of coals used by this company. To meet this objection, the Waldenburg muffle was constructed of 1-millimeter thick sheet iron, which during the coking test bulged to a greater or less degree and thus indicated the magnitude of the expansion pressure of the coal. The charged muffle was placed in an electric Bähr⁶³ oven, which had been preheated to 900° C at its center. A temperature of 900° C was maintained for an hour. To avoid ashing of the coke surface the muffle and contents were allowed to cool in the oven. Expansion of the coal was found to be independent of, and shrinkage dependent on, the time of heating. Expanding coals strongly bulged the walls of the muffle.

⁶⁰ Baum, K., *Glückauf*, **66**, 185–91 (1930); *Fuel*, **9**, 492–4 (1930).

⁶¹ Baum, K., and Heuser, P., *Glückauf*, **66**, 1497–1502, 1538–44 (1930); *Fuel*, **10**, 51–64 (1931).

⁶² Hofmeister, B., *Glückauf*, **66**, 325–32, 365–72 (1930); *Arch. Eisenhüttenw.*, **3**, 559–69 (1930).

⁶³ Bähr, H., *Brennstoff-Chem.*, **5**, 365–71, 384–8 (1924).

The extent of shrinkage could be judged from the amount of contraction of the coke away from the walls of the muffle. This method, like the crucible test, gave no numerical data but, presupposing enough experience, provided useful results for industry.

Hofmeister⁶² compared the results of the Waldenburg muffle test on 9 coals, whose volatile content ranged from 19.3 to 26.8 percent, with the expansion pressure curves as determined by the Kortendamm apparatus.³ Fair correlations were found between the magnitude of bulging of the muffle and the expansion pressure and between the shrinking of the coke away from the muffle walls and the percentage of shrinkage shown by the expansion-pressure curve.

Broche and Nedelmann⁶⁴ coked separately 60-kilogram samples of bright and dull coals, each in steel boxes, for 24 hours at a wall temperature of 1,000° C. The bright coal gave an excellently fused silver-gray coke, fine-grained in structure. The coke from the dull coal was not fused and was in the form of large, comparatively friable, dark gray lumps, in which the individual coal grains could still be detected.

Hoehne⁶⁵ made box tests of coals from the Lower Silesian, Westphalian, Saarland, Saxony, and Upper Silesian districts. The coal charge in the individual tests was kept constant in respect to moisture content, grain size, ash content, and carbonizing time. The strength of the coke made in the box tests, as determined by the "standard trommel" test, was always about 2 to 3 percent lower than that of the corresponding coke taken directly from the oven chamber.

⁶⁴ Broche, H., and Nedelmann, H., *Glückauf*, **68**, 769–79 (1932).

⁶⁵ Hoehne, K., *Glückauf*, **75**, 941–5 (1939).

DILATOMETER AND PENETROMETER TEST
METHODS—COAL UNDER "NO LOAD"
OR KNOWN ADDED LOAD

By the term "load" is understood a weight added to the part of the apparatus normally bearing on the top of the coal charge. The dilatometer and penetrometer test methods employ somewhat the same test principle. The dilatometer (or laboratory "expansion") method uses a piston whose upward and downward movements during the test are measured, whereas the penetrometer method employs a needle or wire loop whose depth of penetration into the softened, heated coal charge is determined. In the dilatometer test the expansion (or contraction) of the heated coal charge is indicated by the vertical displacement of the superimposed piston; in the penetrometer test the softening of the coal mass is judged from the depth of penetration of the needle. The chief differences between test results obtained by the two methods arise from effects caused by the relative cross-sectional areas of the parts of the apparatus that bear on the coal sample. Depending upon the particular original or modified dilatometer test method concerned, the piston head superimposed upon the coal sample may have the same or different shape, and also the same, a larger, or a smaller cross-sectional area than that of the top of the coal charge; its end may be either flat or rounded, and it may be counterbalanced or under a constant or variable load during the test. At high pressure or with the more fluid coals the dilatometer piston head may even penetrate the softened coal, similar in some degree to what is observed with or without a loaded needle or wire loop in the penetrometer test method. Sharp distinctions between the principles of operation in the two methods, therefore,

cannot always be made. These two test methods do not measure the actual magnitude of the pressure or stress developed in the heated coal mass during its carbonization.

DILATOMETER TEST METHODS

Publications describing original, modified, or adapted dilatometer methods show a wide diversity in the details of the construction of the apparatus and in the test procedures. Lessing¹³ devised the first dilatometer method for determining swelling of coal during heating that allowed more accurate observation than was possible by coking in a crucible test. His original apparatus consisted of a coal tube encased in a similarly shaped quartz retort tube, which was held vertically and heated electrically by an outside winding of platinum resistance wire. A flat-bottom quartz piston tube fitted loosely inside the coal tube and slightly compressed the coal sample. A constant or variable load, as desired for the particular test, was obtained by introducing various amounts of quartz powder into the piston tube or by changing its length. Generally, however, a constant load was used throughout a given test. Lessing observed that "higher pressure tended to form more swelled coke than the lower pressure." Twenty different samples of coal were tested, apparently heated to 900° C in 5 to 7 minutes. Lambris⁵¹ stated that the method was objectionable, for a complete interpretation of the results, because the ratios of volume of coke to volume of coal must be determined.

Further studies were made by Lessing⁶⁸

⁶⁸ Lessing, R., *J. Gas Lighting*, **118**, 855-61 (1912); *Trans. Inst. Gas Engrs.*, **10**, 242-55 (1912); *Iron & Coal Trades Rev.*, **84**, 1034-5 (1912); *Gas World*, **56**, 842-9 (1912); *Orig. Com. 8th Intern. Congr. Applied Chem.*, **10**, 195-8 (1912), **27**, 78 (1912); *Trans. J. Chem. Soc.*, **117**, Pt. 1, 247-56 (1920); *Fuel*, **2**, 152-5, 186-90 (1923).

upon such factors as: (a) different mesh sizes of coal; (b) duplicate heating tubes, one for temperature measurements by a thermocouple, the other with a side neck at different heights to permit collection and study of the volatile products of distillation; (c) adjustable silica supports to move the heated assembly to different desired heights in the electric furnace; and (d) different end temperatures and total heating periods.

Schreiber⁶⁷ has also followed the principle of Lessing. Real distinction in the expanding properties of 7 coals and blends tested could not be made because of the very small displacement of the weighted iron piston measured in millimeters.

Charpy and Durand⁶⁸ made a small cylinder of finely ground coal moistened with water. The briquet was dried at 105° C and placed in a vertical glass tube of slightly larger diameter. A glass rod, whose top end was drawn out and bent at a right angle to act as a pointer before a scale, was superimposed on the top end of the briquet. The contraction or expansion of the coal cylinder was observed as a function of temperature. The coal cylinder first showed a progressive contraction up to a maximum. Softening of the coal cylinder completely filled the annular space in the glass tube. The authors defined this "maximum initial contraction" as the "fusion temperature" of the coal. The sample next showed an apparent increase in volume, sometimes very large, due to the formation of gas bubbles within the melted mass; and, finally, this increase was followed by a second contraction with the formation of coke. Eight French coals were tested. The fusion point was found

to be independent of the volatile-matter content or other constituent of the proximate analysis and was characteristic for each coal. The fusibility, as well as the capacity for coking, was observed to be directly related to the state of oxidation; coals oxidized at 120° C could no longer be fused.

Audibert⁶⁹ compressed powdered coal, moistened with water, to a uniform density in a steel mold to form a truncated cone. The briquet was placed in a cylindrical copper or iron tube of slightly larger diameter, which was supported vertically in a lead or salt bath. A counterpoised glass rod rested on top of the briquet. The top of the rod formed a pointer, which moved before a scale. For a given weight of coal and fixed values of the diameters of the coal cylinder and the dilatometer tube, the change in shape of the heated coal was found to depend on the rate of heating. Tests were carried out according to two heating programs: (a) *sudden or rapid heating* in which the dilatometer assembly containing the coal was plunged into the preheated bath at selected temperatures ranging from 370 to 600° C, and then this *selected temperature T* was maintained for the test; and (b) *progressive heating* at definite rates, from $\frac{1}{3}$ to 3° C per minute.

The results from program (a) were plotted, using as abscissas the time in minutes from the instant of immersion of the dilatometer assembly, and as ordinates the vertical displacements of the pointer, expressed as percentages of the initial length of the coal cylinder. The family of curves obtained for the different selected temperatures showed the same general character-

⁶⁷ Schreiber, F., *Stahl u. Eisen*, **40**, 1278-9 (1920).

⁶⁸ Charpy, G., and Durand, J., *Compt. rend.*, **171**, 1358-60 (1920).

⁶⁹ Audibert, E., *Rev. ind. minérale*, **6**, Pt. 1, No. 126, 115-36 (1926); *Fuel*, **5**, 229-44 (1926), **6**, 185 (1927). Audibert, E., and Delmas, L., *Rev. ind. minérale*, **7**, Pt. 1, No. 145, 1-22 (1927); *Fuel*, **6**, 131-40, 182-9 (1927), correction, both references, *Fuel*, **8**, 232-3 (1929).

istics. At all temperatures below a certain value T_r , the temperature at which melting began with rapid heating, or "softening point," the pointer remained motionless. For all temperatures between T_r and T_g , a higher second temperature above which rapid heating caused an expansion or apparent increase in volume of the coal, designated the "intumescence point," the pointer moved downward. The "intumescence" was caused by the formation within the mass of heated coal of a very large number of small gas bubbles. The ratio, C_T , of the total downward movement to the initial length of the coal cylinder increased with temperature throughout the temperature interval T_r to T_g for a given coal and a given size dilatometer tube. When the temperature of the bath was above T_g , the pointer at first descended but later rose, the amplitude of the upward movement increasing with temperature. At temperatures very little above T_g , the pointer came back to a level well above its initial position.

When a coal was heated rapidly to a temperature between T_r and T_g , the value of C_T , as defined above, depended on the value of the ratio of the diameter of the coal cylinder to the inside diameter of the dilatometer tube. When the coal cylinder fitted the tube exactly, C_T had a very low value, regardless of temperature. With increasing differences in diameter, the value of C_T increased with the volume of the annular space between the coal and the tube. For temperatures just below T_g the value of C_T corresponded to a volume of tube not appreciably different from the volume of coal. These observations meant that the coal, when heated to such temperatures, was fluid enough to fill, by the action of gravity, the empty space between the coal and the walls of the dilatometer tube. That the coal did not undergo a sharp

fusion was indicated by the increase with the temperature T of the relative depression C_T , observed at different temperatures with the same coal and the same apparatus.

Between the temperature T_g , as defined above, and another temperature T_s , always below 600° C, the apparent increase in volume of the heated coal mass became greater as the temperature to which the coal was rapidly heated was increased. A coal heated rapidly to or above this temperature T_s and then cooled could not be melted again, no matter what the aftertreatment. This *solidification temperature* T_s might even lie between T_r and T_g , if the coal had been maintained long enough between these temperatures. The time required ranged from less than 1 hour up to 120 hours for 12 coals tested. Under such conditions, the coal would ultimately solidify even if the temperature was never allowed to fall below the initial softening temperature T_r . With rapid heating of 24 different coals, the temperatures T_r and T_g varied, within wide limits, from 325 to 450° C for T_r and from 375 to 500° C for T_g . No simple relationship was observed between these temperatures and the chemical composition as determined by the usual methods.

As stated above, the coal once melted and resolidified could not be remelted, no matter what the aftertreatment, even if the temperature was brought up to and maintained above T_r . "In other words, the fusion is of a *transient* nature, the duration of which is inherently limited." This transient fusion of coal was compared to that of chemical substances, such as potassium chlorate or sulfur, both of which undergo a change on heating into more refractory products. Similarly, by the action of heat, coal undergoes chemical changes, the exact nature of which is un-

known, and gives a new mixture of residual products of higher melting point.

By *progressive heating* (program b) it was found that with like heating rates the thermal decomposition point T_p may be below the softening point T_r for some coals and above T_r for other coals. Audibert designated the latter as *first-class coals*. For such coals, the softening points and the intumescence points obtained by *progressive* heating at 1° C per minute were 25° C lower, on the average, than similar points obtained by *rapid* heating.

Davies and Wheeler⁷⁰ repeated the work of Audibert, by the same test method and with some of the same coals. Particular attention was paid to the reactions between the fusible and nonfusible portions of the coals. Davies and Wheeler, in contrast to the results of Audibert, found: (1) at all bath temperatures below the softening temperature of the coal T_r , the pointer remained motionless; (2) at all temperatures between T_r and the higher intumescence temperature T_g , the pointer moved downward and continued to do so for some time; and (3) at temperatures higher than T_g , the pointer first ascended and then descended. Davies and Wheeler concluded that, if the coal had melted and flowed by gravity to fill the tube completely as stated by Audibert for complete "melting" of the coal, "the percentage contractions should increase progressively with increased difference between the diameter of the coal pellet and that of the tube." Their tests on 5 coals used by Audibert showed that no one of these coals contracted enough to reach the theoretical value of 54 percent contraction necessary with the size of pellet and tube employed, even if the coals had melted and flowed so as to fill the tube completely. They believed that "the re-

sults obtained by Audibert, from which he deduced complete fluidity of the coal pellets on heating, appear to have been due to the accidental choice of dimensions of the pellets and dilatometer tubes, the coals becoming sufficiently plastic to flow a short distance under load." In answer to these findings, Audibert,⁷¹ calling attention to his publication⁷² in which he made definite reservations of his earlier view⁶⁹ on the complete "melting" of coal, stated: "In short, I ignore the problem as to whether the fusion of coal is complete or whether it is only partial."

Arnu⁷³ used the dilatometer method of Audibert and Delmas.⁶⁹ Since the briquet average diameter of 6.5 millimeters was smaller than that of the tube, the piston fell when the coal fused. On the assumption that the apparent volume of the melted mass was equal to that of the original coal briquet, the theoretical height of the fall of the piston would have been 34 percent of the initial height of the briquet. In general, a contraction less than this was obtained. The change in length of the coal during heating as shown by the movement of the piston gave observations similar to those made by Charpy and Durand.⁷⁰ The percent changes in volume (length) were plotted against temperatures, and from the curves obtained the melting and solidifying points of different coal were determined. Arnu⁷⁴ later modified his procedure to use a cylindrical pellet of coal instead of the truncated cone of the same average diameter.

⁷¹ Audibert, E., *Fuel*, **10**, 189-90 (1931).

⁷² Audibert, E., *Rev. ind. minérale*, **9**, Pt. 1, No. 194, 151-87 (1929); *Fuel*, **8**, 225-43 (1929).

⁷³ Arnu, C., *Rev. ind. minérale*, **13**, No. 296, 155-73 (1933); *J. usines gaz*, **57**, 512-19, 541-8 (1933); *Chaleur et ind.*, **15**, No. 167, 278-96 (1934).

⁷⁴ Arnu, C., *Chimie & industrie*, **32**, Nos. 2-3, 276-92, 530-40 (1934).

⁷⁰ Davies, R. G., and Wheeler, R. V., *Fuel*, **10**, 100-8 (1931).

Pieters, Koopmans, and Hovers⁷⁵ determined the softening temperatures and swelling properties of coking coals by a modification of the dilatometer method of Audibert. A double-hole furnace enabled determinations to be made in duplicate. A coal which did not swell under the test conditions was not considered suitable for metallurgical purposes. Good coking coals showed a swelling of 50 to 150 percent.

Cassan⁷⁶ recognized the complications arising in test methods that used coal pellets possessing some voids. Accordingly, he compressed his coal samples to maximum density. The charged retort was heated in an electric tube furnace, encased in a polished nickel-brass jacket to minimize heat losses. The furnace could be regulated to give heating rates of 10, 5, 2, or 1° C per minute from 350 to 500° C. The 2° C per minute rate was considered standard. Swelling curves showing expansions, expressed as percentage of the initial coal volume, were plotted as ordinates against degrees Centigrade as abscissas.

Cassan also studied the fusion of loosely packed coal. Results similar to those of Audibert and Delmas⁶⁹ and of Arnu^{73, 74} were obtained for the beginning of fusion, but, in addition, there also were observed a phase of relative fluidity and a second sinking of the piston, subsequent to the first swelling. These results were plotted in like units on the same diagrams giving the swelling curves as determined for the densely compressed briquets. Differences in the courses of the two sets of curves were explained in terms of the effects of voids in the coal samples used for the

fusion-curve determinations. Mathematical treatment of the data obtained in the two types of test and of the values for real and apparent densities of the coals gave a rough criterion for estimating the results to be expected in practice, particularly in the correct choice of blends for coking.

Chandesris⁷⁷ employed the method of Audibert in a study of Saar coals. The heating rate used was 5° C per minute up to 325° C and 2° C per minute from 325 to 500° C. Curves constructed according to those of Audibert and Delmas showed that: (1) coals with sufficient expansion after melting as a rule gave a satisfactory caked coke; (2) partly melted coals with feeble expansion have doubtful coking value; and (3) coals that do not expand during heating, in general, do not produce a caked coke.

It was suggested that the tests be repeated at lower heating rates, for example, 1 or 1.5° C per minute, to determine the heat-sensitive properties of the coals in relation to their plasticity. The beginning of softening was defined as the temperature at which the shrinkage of the test briquet amounted to 10 percent, whereas the beginning of expansion represented the temperature at which the expansion amounted to 10 percent of the original length of the test briquet. These temperatures, together with other important temperatures defining the rate of degasification, were discussed for Saar coals and the residues left after their extraction with tetralin, or with tetralin and pyridine extraction, or by treatment with quinoline.

The Chemical Department of the South Metropolitan Gas Company⁷⁸ employed a dilatometer method similar in principle to

⁷⁵ Pieters, H. A. J., Koopmans, H., and Hovers, J., *Congr. intern. mines, mét. géol. appl.*, 7th Sess., Paris, 1935, *Mines Sect.*, 2, 496-506; *Rev. ind. minérale*, 16, No. 376, 880-90 (1936).

⁷⁶ Cassan, H., *Chaleur et ind.*, 16, 495-508 (1935); *J. usines gaz*, 60, 145-57 (1936).

⁷⁷ Chandesris, R., *Rev. ind. minérale*, 16, Pt. 1, No. 361, 1-20, No. 365, 243-78 (1936); see also Hoffmann, H., *Glückauf*, 73, 219-26 (1937).

⁷⁸ South Metropolitan Gas Company, *Chem. Dept.*, *Fuel*, 15, 36-9 (1936).

that of Audibert. The apparatus, however, permitted simultaneous duplicate determinations to be made under identical test conditions at temperatures above 600° C. Heating was carried out in a drilled block of heat-resisting steel by carefully controlling the gas supply by means of an ingeniously devised gas thermostat. The vertical displacement of the piston in each coal tube was recorded automatically by two pens on charts mounted on two revolving drums. Presumably, a heating rate of 1.67° C per minute was used after the bath had been preheated to 350° C. Four characteristic temperature points, namely, softening or starting temperature, intumescence temperature, hardening temperature, and temperature of aftercontraction, were selected from the piston movement-temperature relationships. The total linear expansion observed between the intumescence and hardening temperatures was termed the "swelling index." The results obtained showed but little correlation with those of actual practice, but the apparatus and test method were considered preliminary to more refined work.

Jackson⁷⁹ used a vertical, transparent silica tube containing a small briquet of air-dried coal. Small differences in briquetting pressures did not affect the results. The tube was encased in an outer transparent silica tube, which was wound with resistance wire for heating and fixed in place by two rows of small pieces of silica fused along opposite sides of the tube. This wider tube served as a heat insulator. A silica or glass rod piston, which acted also as an index before a scale, rested on top of the briquet. The heating rate was controlled at 10° C per minute. The test was conducted in vacuum and was completed in 1 hour. All

coals tested showed very gradual rates of expansion, less than 0.05 inch up to their fusion. At the fusion point very sudden expansion took place and proceeded rapidly until plasticity ceased. Subsequent heating caused gradual shrinkage. Fourteen coals, ranging in volatile-matter content from 31.5 to 35.7 percent (as-determined basis), were tested. The following conclusions were drawn: (1) melting points and plastic temperature ranges were characteristic of the coal; (2) standard test conditions, in particular, the rate of heating, were emphasized to govern the extent of the decomposition of the coal prior to its fusion; (3) oxidation, if carried far enough, rendered the coal nonfusible, although partial oxidation by exposure to air did not affect the fusion point, but reduced the plastic range and the percentage of expansion; (4) within limits, variations in ash affected the plastic range and the percentage of expansion but did not affect the fusion point; and (5) coals with short plastic ranges were accompanied by low expansion and were easily carbonized in vertical retorts, whereas those with long plastic ranges gave trouble. These observations were affected by the size of the coal.

Bradley and Mott⁵⁰ devised the original Sheffield laboratory coking test for measuring softening and swelling temperatures and degree of swelling of coal. The swelling power of the coals tested bore a general relationship to their value for coke-making.

The Sheffield laboratory coking test was later "standardized."^{80, 81} Readings of temperature and plunger movement were made at intervals of 5 minutes after a temperature of 300° C was reached. The

⁸⁰ Mott, R. A., and Wheeler, R. V., *Trans. Inst. Mining Engrs. (London)*, **84**, 29-42 (1932-33); *Colliery Guardian*, **145**, 797-800 (1932).

⁸¹ Davies, R. G., and Mott, R. A., *Fuel*, **12**, 294-303 (1933).

⁷⁹ Jackson, J. A., *Gas World*, **90**, 715-7 (1929); *Gas J.*, **186**, 863-5 (1929).

vertical movement of the pointer at the *temperature of initial contraction* of the coal charge was less than 0.1 millimeter, and in the succeeding 10 minutes it was only about 0.25 millimeter. With experience this movement could be observed without the use of magnification. After the first 10 minutes of slight contraction, the subsequent movement of the pointer was very marked and the direction was reversed suddenly at the temperature of *initial expansion*. *Final expansion* also ended suddenly. Near the temperatures of initial contraction, initial expansion, and final expansion observations were made every minute. The authors stated that, for the same coal sample, the temperature of initial contraction was reproducible to 3° C; the temperature of initial expansion within 1° C; and the temperature of final expansion to 3° C.

Davies and Mott⁸² found that the plasticity of coal, when heated under conditions of the standardized Sheffield test (permitting some expansion), ended at a lower temperature than when heated under conditions that prevented expansion. For example, the plastic range of Two Foot Nine Seam coal ended at about 480 and 520° C, respectively, under the two conditions of test.

Lambert⁸³ used the Sheffield laboratory coking test apparatus to study the effect of destructive oxidation of coal caused by prolonged heating at 105° C in a water-jacketed oven. After 24 and 48 hours' heating, a strongly coking, highly swelling coal (Gray-Campredon agglutinating index of 23) showed definite increases in the temperatures of initial contraction, initial expansion, and final expansion. The agglu-

tinating index and the percentages of contraction, of total expansion, and of net expansion were reduced markedly. A moderately coking and swelling coal (agglutinating index of 16) under the same conditions showed no appreciable changes, except for a 5 percent reduction in expansion.

To study the effects of varying proportions of ash, tests were made on coals before and after the addition of coal-shale ash. A series of samples of increasing ash content was prepared by adding shale, previously burned to ash, to the cleaned coal. Test results in the Sheffield apparatus showed that contraction was not affected, but that the total and net expansions were greatly reduced. The data were used to adjust the ash content of coking charges for blast-furnace coke. More than 100 tests on South Wales and Monmouthshire coals and blends were made. In general, the temperatures of initial contraction decreased as the swelling propensities of the coal increased. No definite relationship was observed between agglutinating index and percentage of *net expansion*. Expanding coals with carbon content between 88.4 and 84.9 percent (basis not given) produced the best cokes. The carbon-to-hydrogen ratio, between 17 and 19, neared the maximum. With two exceptions, coals showing less than 25 percent net expansion and with an ash content not over 7 percent, when coked alone, were not satisfactory for the production of blast-furnace coke. The two exceptions had fairly high agglutinating indexes. The coking tests were carried out in an experimental coke oven similar to that of the Midland Coke Research Committee.

Tests on South Wales coals indicated that, where it was not possible to test a cleaned sample of coal, an allowance of 12 percent expansion should be added for each 1 percent of ash above 7 percent,

⁸² Davies, R. G., and Mott, R. A., *Fuel*, **12**, 371-82 (1933).

⁸³ Lambert, J. L., *Gas World*, **102**, No. 2644, *Coking Sect.*, 44-6 (1935); *Colliery Guardian*, **150**, 715-6 (1935).

the value taken as the works standard. For lower-ash coals, a reduction of 12 percent expansion should be made for each 1 percent of ash under 7 percent.

Brooke, Walshaw, and Lee⁸⁴ determined the swelling power of 25 coking slack coals by the standardized Sheffield laboratory coking test. The average contraction, average gross expansion, and average *net expansion* values were expressed in percentages. The average net expansions recorded for some coals were not the differences between the corresponding recorded gross expansions and contractions. The authors stated that this was due to the fact that particular coals in some tests gave a zero figure and in other tests a positive figure. Just how they arrived at the recorded *average net expansion* percentages for these coals, however, was not evident. Some coals, particularly those with zero net swelling index, had what the authors called a negative effect when mixed with other slacks; that is, the resultant swelling figure for a blend of two coals may be considerably below the mathematical average of those of the two individual coals. The difference between the calculated and experimental index was not so noticeable in strongly swelling slacks as in moderately or poorly swelling slacks. A general relationship was found between the experimental swelling index (percent net expansion) of the coal or blend used for carbonizing and the shatter index of the resultant coke. Considering the fact that the coals tested were from 22 different collieries and that some of these slacks were not of suitable quality for the production of blast-furnace cokes, the correlations found were remarkably good.

⁸⁴ Brooke, W. J., Walshaw, H. R. B., and Lee, A. W., *J. Iron Steel Inst. (London)*, **134**, No. 2, 287-325P (1936); *Colliery Guardian*, **153**, 567-70, 620-3 (1936).

Mott and Spooner⁸⁵ recognized the disadvantages of fragility, high cost, delays in obtaining spare parts, and unavoidable temperature differences between the outside and inside of the standardized apparatus used in the Sheffield laboratory coking test and have improved the construction features to overcome these defects.

Comparative tests of loosely charged coal in both silica and steel tubes, each heated in an electric furnace at 1° C per minute, showed swellings of 92 and 104 percent, respectively. The softening temperature of the coal in the steel tube, measured outside, was 29° C higher than that of coal similarly determined in the silica tube. Other characteristic temperatures also were higher. This steel tube was similar to that used by the South Metropolitan Gas Company.⁸⁰ To overcome the effect of the greater heat conductivity of the steel tube (above that of silica), a new retort was constructed of cold-drawn, seamless, 1/4-inch steel with ends recessed to accommodate top and bottom push-on caps of mild steel. The retort was encased in a close-fitting aluminum liner which, in turn, fitted easily in a standard Gray-King electric furnace.

The retort was charged with coal compressed to a void space of 33 percent. The temperature of the furnace was raised quickly to 300° C and then controlled at 1° C per minute. Readings were taken at 1-minute intervals near the temperature of initial contraction, initial expansion, and final expansion. With coals of low swelling power, there was no movement of the pointer after the temperatures of *final expansion* had been reached, until at a very much higher temperature, when there was a slight shrinking of the charge. With coals of high swelling power, the plunger

⁸⁵ Mott, R. A., and Spooner, C. E., *Fuel*, **16**, 4-14 (1937).

began to sink through the charge at a temperature a few degrees above the final expansion, and came to rest at a somewhat higher temperature, usually before it had sunk to the bottom of the charge. The extent of the fall of the plunger was suggested as an index of the plasticity developed by the coal. The percent contraction of the coal was calculated by dividing the difference between the maximum pointer scale reading and that observed at the initial contraction temperature by the height of the coal column and multiplying by 100. The percent gross expansion was obtained by dividing the difference between maximum and minimum scale readings by the height of the coal charge and multiplying by 100. The authors preferred gross expansion; some other earlier users of this test apparatus have made use of the net expansion, that is, gross expansion minus contraction.

Schlöpfer and Müller⁸⁶ prepared a pellet from powdered coal (grain size, 0 to 1 millimeter) and placed it in a platinum crucible, which was set in the bottom of a cold electric furnace. A glass rod piston, supporting a distance gage and a 500-gram weight, was superimposed on the pellet. During heating, a slow stream of carbon dioxide was passed around the pellet. The beginning of softening was indicated by the marked evolution of gases and vapors. The softening temperature was taken as the first significant movement of the piston. Softening points were determined for 4 coals before and after preheating at 200° C for 30 minutes with subsequent cooling in air. Three of the preheated coals—Neumühl, Heinitz, and La Houve—showed significantly higher softening points

and more abrupt changes than the same coals in the original condition. The fourth coal, Boltigen, rich in plastic constituents, had to be preheated at 250–280° C to cause similar behavior. Preheating the coals to only 150° C did not affect their normal behavior.

Schlöpfer and Müller also made a direct determination of the degree of swelling. They used a furnace that was claimed to give unidirectional heating from the sides. Tests were carried out on a large number of coals, the results on 4 of which (Boltigen, Neumühl, Heinitz, and La Houve) were plotted with “swelling time in minutes” and “core temperatures of the coal” as ordinates against “degrees Centigrade” as abscissas. The curves were discussed according to three arbitrarily chosen segments: the first, between 350 and 400° C, during which softening of the coal took place; the second, around 400° C, at which strong decomposition of the coal substance and a considerable increase in volume were shown; and the third or horizontal part of the curve representative of the end condition with continued degasification. The authors studied the dependence of the degree of swelling on the rate of heating and the influence of preheating on the swelling capacity of the coal. These results were compared with those of crucible swelling tests, such as those by Bochum’s method.

The U. S. Bureau of Mines⁸⁷⁻⁹¹ has de-

⁸⁷ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **344**, 14-9 (1931).

⁸⁸ Davis, J. D., Jung, F. W., Juettner, B., and Wallace, D. A., *Ind. Eng. Chem.*, **25**, 1269-74 (1933); *Mining Met. Investigations, U. S. Bur. Mines, Carnegie Inst. Tech., Mining Met. Advisory Boards, Coöper. Bull.* **60** (1933), 17 pp.

⁸⁹ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph* **5**, 106-9 (1934).

⁹⁰ Brewer, R. E., and Atkinson, R. G., *Ind. Eng. Chem., Anal. Ed.*, **8**, 443-9 (1936).

⁹¹ Brewer, R. E., and Triff, J. E., *Ind. Eng. Chem., Anal. Ed.*, **11**, 242-7 (1939).

⁸⁶ Schlöpfer, P., and Müller, E., *Eidgenöss. Materialprüfungsanstalt, E. T. H. Zürich, Ber.*, **55** (1931), 47 pp.; *Schweiz. Ver. Gas- u. Wasserf. fach., Monats-Bull.*, **11**, 201-11, 358-60, 365-82 (1931), **12**, 9-23 (1932).

veloped the well-known Agde-Damm dilatometer test method, so named on account of the incorporation of certain construction features of the apparatus and procedure of the penetrometer test methods of Damm³ and of Agde and Lyncker.² During the ten years of nearly constant use in research investigations and routine testing of bituminous coking coals, the original Bureau of Mines Agde-Damm test method has undergone a number of modifications, in both apparatus and test procedure, described in the papers cited.

The K-B-S apparatus of Shimomura⁵ was based upon the softening zone apparatus of Kattwinkel¹⁹ and the recording arrangement of Baum,⁹⁴ hence the name K-B-S. Eleven Japanese and Chinese coking coals were tested. Under "no load" (piston not weighted) the initial point of expansion, though varying with different coals, was definite in each case, whereas the end point of expansion, near the resolidification point, differed somewhat in duplicate tests on the same coal. With an added load on the piston the initial and end points of expansion were lower and the net expansion was less than values determined under "no load." Additional temperature-volume characteristics were noted, usually for the beginning of contraction and the end of "penetration." The temperature difference, in degrees Centigrade, between the beginning of contraction and initial expansion, was designated as "contraction range," that between initial and final expansion as "expansion range," and that between final expansion and end of penetration as "penetration range." The flat part of the curve or

"equilibrium range" represented the equilibrium between the surface tension of the molten coal, or its viscosity, and the penetrating action of the weighted piston.

Shimomura⁵ later used his K-B-S apparatus in a study of blending coals for coke manufacture. Seventy-six samples of Yubari and Hashima coals were blended with 10, 20, 30, 40, and 50 percent of (a) anthracite, (b) coking coal, (c) high-volatile highly oxygenated coal, (d) oxidized coal, (e) 450° C semicoke, (f) 500° C semicoke, (g) coke breeze, and (h) quartz sand, respectively. The initial expansion temperatures of the coals were raised and the total magnitudes of the expansion were lowered most by 450° C semicoke, next by anthracite and 500° C semicoke, then by coke breeze, oxidized coal, and the two coals (b) and (c), and least by quartz sand. Blending with the coking coal gave increased viscosity. The data were correlated with those for ash, volatile matter (dry basis), phenol extract, carbon, hydrogen, and oxygen (all on a dry, ash-free basis), expansion pressures made in a Nedelmann apparatus,⁹⁵ and gravimetric volatile-matter data obtained in Shimomura's automatic-indicating type balance developed during the investigation. Desiderata for ideal coking coals in terms of numerical data for the properties just cited were formulated.

Later, Shimomura⁵ classified coals into groups from the forms of their K-B-S curves as shown on the next page.

Data on 20 samples of English coals and blends were not complete. Two coals, "M" (Brancepeth Mine, Three Quarter Seam [Durham], unwashed run-of-mine) and "E" (Grassmoor Mine, Tupton Seam [Derbyshire], unwashed slack), were placed

⁹² Agde, G., and Lyncker, L. von, *Brennstoff-Chem.*, **10**, 86-7 (1929).

⁹³ Shimomura, A., *J. Fuel Soc. Japan*, **11**, Sect. 1, 184-9, Sect. 2, 17-9 (in English) (1932); *Fuel*, **11**, 340-3 (1932).

⁹⁴ Baum, K., *Glückauf*, **64**, 1733-41 (1928).

⁹⁵ Shimomura, A., *Fuel*, **13**, 262-8 (1934).

⁹⁶ Nedelmann, H., *Brennstoff-Chem.*, **12**, 42-3 (1931).

CLASS	SWELLING	EXPANSION percent	VISCOSITY	COKING PROPERTIES
Ia	Excessive	More than 400	Low	Often finery and weak cokes
Ib	Excessive	More than 400	High	Good (coal possibly dangerously expanding)
IIa	High	100-400	Low	Often finery and weak cokes
IIb	High	100-400	High	Generally good
IIIa	Moderate	50-100	Low	Often finery and weak cokes
IIIb	Moderate	50-100	High	Generally good
IV	Not appreciable	Less than 50		Caking
V	None			Imperfectly caking
VI	None			Noncaking

in Classes I and V, respectively. Apparently, the K-B-S curves, determined without a weight on the piston, were used because the Durham coal showed an expansion of 435 percent under this condition and only 152 percent in the test with a load of 74.5 grams per square centimeter. The analyses of the Durham coal (dry basis) were 30.2, 4.7, and 65.1 percent, respectively, for volatile matter, ash, and fixed carbon, and of the Derbyshire coal 37.9, 7.4, and 54.7 percent, respectively, for these constituents.

PENETROMETER TEST METHODS

Lierg⁹⁷ apparently was the first to determine the softening point of coal by a penetrometer method. A freshly cut, rectangular section of coal of equal length and width and approximately 0.5 to 1 millimeter thick was supported horizontally within a vertical, transparent quartz tube of suitable diameter. The point of a uniformly loaded, metallic needle rested at the middle of the coal section. Trial tests were made to establish the exact manner of loading. A thermocouple within the tube measured (1) the softening temperature, that at which the coal sample began to sag; (2) the coking temperature at the beginning of deformation; and (3) the

temperature of eventual penetration of the weighted needle through the coal. Nitrogen gas, preheated to the temperature of the tube, was passed through the apparatus during the test. Accurate and duplicable results were claimed. The method was suggested as a means of determining the properties of coals for classification purposes.

Greger⁹⁸ studied the softening of coal during heating by measuring the depth of sinking of a loaded loop of wire into a cylindrical briquet of coal. Rates of sinking of the wire loop, in millimeters per minute, plotted as ordinates against degrees Centigrade as abscissas expressed the measures of viscosity for the different coals. The original apparatus proved suitable only for coals softening with extreme difficulty. For easily softening coals the wire loop sank through the coal too rapidly for measurement. The apparatus accordingly was modified so as to permit a constant or controlled rate of sinking of the wire loop into the coal. The beginning of softening was taken as the first sinking down of the wire loop. The degree of softening increased with rising temperature to a maximum softening temperature and then decreased. The loads necessary to force the wire loop into the coal a fixed depth per unit of time were plotted as ordinates

⁹⁷ Lierg, F., *Z. angew. Chem.*, **35**, 264-8 (1922); *Am. Gas J.*, **118**, 63-6, 74-7 (1923).

⁹⁸ Greger, H., *Braunkohlenarch.*, No. 9, 67-106, esp. 78 et seq. (1925).

against degrees Centigrades as abscissas. These softening curves and the maximum softening temperatures varied with different types of coal. For any particular type, the softening curve and the appearance of the semicoke were affected by preheating the coal, its preheating temperature, and the duration of heating. Furthermore, the softening and swelling properties of the coals were depreciated by storage in the absence of air after preheating.

Meyer²⁹ used the wire loop penetrometer method of Greger⁹⁸ to determine the softening behavior of 6 German coals. Determinations were made on: the original coals; coals preheated for 3 hours at different temperatures, below, within, and above their plastic temperature ranges; coals heated at different rates; and samples after extraction once or repeatedly with benzene at different temperatures and pressures for varying times followed by different methods of drying. Results of these determinations were correlated with those from Muck crucible tests, and conclusions were formulated on the coking power of the coals.

Damm³ determined the fusion temperature of 6 different coals by measuring the penetration of a pointed iron tube into a coal pellet. A thermocouple was held within the tube, the hot junction being located at the tip of the tube. The furnace was heated fairly rapidly to 350° C and gradually thereafter at an unspecified rate in stages of 10° C. The fusion temperature was taken as that corresponding to the beginning of movement of the pointer over the scale, namely, the time at which the pointed tube began to sink into the coal. Check results within 5° C were claimed, which Damm considered accurate enough for routine evaluation of the coking properties of a coal.

Lambris⁹⁹ used the method of Damm³ to determine the softening points of 12 coking coals from the Rhenish-Westphalian district, containing 17.37 to 26.04 percent volatile matter (dry, ash-free basis). Softening temperatures ranged from 390 to 425° C but were not in the same relative order as the ranks of the coals. After storage for 4 months in closed bottles, from which air had not been entirely removed, the softening points of 2 very strongly expanding and 2 feebly expanding coals were increased 75 to 90° C. The author explained the higher softening temperatures as due to the melting of secondary bitumens whose presence in the coal and whose melting points had no decisive effect upon caking index, degree of swelling, or expansion pressure of the coals; these last three properties did not change after the 4-month storage period.

Melzer¹⁰⁰ modified the Damm test method. Preliminary tests on 2 coals showed that the temperature of softening was increased 18° C for one coal and 40° C for the second by using pellets that had been loosely and strongly compressed, respectively. The preparation of the briquets in a pellet press used for calorimeter determinations was standardized by having a fixed maximum pressure. The ash content of the coal was found to have no significant effect on the softening temperature. Determinations on 11 coals and 9 binary coal blends, varying by 10 percent increments, showed that their softening points increased fairly regularly with decreasing content of volatile matter. In general, coals with 20 to 22 percent of volatile matter (basis not stated) showed softening points between 400 and 450° C,

⁹⁹ Lambris, G., *Brennstoff-Chem.*, **12**, 181-7 (1931).

¹⁰⁰ Melzer, W., *Arch. Eisenhüttenw.*, **4**, 169-75 (1930).

and coals with 22 to 28 percent of volatile matter gave softening points between 330 and 390° C.

Melzer pointed out that the softening point of a coal blend should be used with the utmost caution in daily works supervision. As a basis for classifying coals to be used in small and large commercial coke ovens, Melzer studied the relationship between the softening points of 24 coals (volatile matter ranging from 19.4 to 28.8 percent, basis not stated) and the results of their "stepwise degasification" according to the method of Damm.³ This method divided gravimetrically the volatile matter according to three temperature zones: (1) up to within 25° C of the softening point of the particular coal; (2) from this temperature to 25° C above the softening point; and (3) above temperature zone (2). These zones were designated "pre-degasification," "softening zone," and "after-degasification," respectively. Good coking coals suitable for use in small coke ovens were those whose volatile matter was distributed as follows: predegasification zone, up to 20 percent; softening zone, 20 to 35 percent; and after-degasification zone, 40 to 65 percent. Expanding coals showed higher predegasification and softening-zone values, accompanied by low after-degasification. Coals with high after-degasification and lower softening-zone and predegasification values, when coked in small ovens and occasionally in wide ovens, formed small-sized fissured cokes.

These conclusions were substantiated by data obtained in large-scale tests in 500-millimeter-wide Otto regenerative chambers. Temperatures, gas composition, and heating value of the gas determined at hourly intervals indicated definite trends for different kinds of coals. The zones of degasification were estimated in "thirds" of the carbonizing time. The course of

the curves representing gas composition showed, in particular, that the break in the hydrogen curve in the third, or after-degasification, zone was characteristic of the particular coal being coked. The maximum percentage of hydrogen occurred usually with simultaneous increases in carbon monoxide and carbon dioxide and was explained as due to the decomposition of hydrocarbons.

Melzer¹⁰¹ later modified the Damm test method further so that the end of softening of the coal sample could be determined by the "feel method." An extension tube about 22 centimeters long, mounted with the aid of an overlapping metal holder set in the space for the coal pellet, confined the softened coal mass and also made it easier to introduce the steel needle. The coal for making the briquet was first ground to pass a sieve of 400-mesh per square centimeter. The temperatures of the beginning and the end of softening were determined for 7 coals with volatile-matter content ranging from 19.59 to 39.72 percent (basis not stated), and for 6 four-component blends of certain of these coals to give blends ranging in volatile-matter content from 22.80 to 24.18 percent (basis not stated). Stepwise degasification tests also were made of these coals and blends by the method of Damm.³ Melzer classified the degree of softening of each coal and blend by numerical values from 0.3 to 5, for which 1 signified very viscous and 5 very soft. It was not stated how these numbers were estimated. Presumably, the estimation was made by the "feel method." The numbers reported appear to have had no dependence on the volatile content, the length of the softening range, or the pre-, main-, or after-degasification weights of volatile matter expelled.

¹⁰¹ Melzer, W., *Arch. Eisenhüttenw.*, **6**, 89-93 (1932).

Agde and Lyncker⁹² developed an apparatus an important feature of which was an electrically heated copper or aluminum block in which two holes were drilled from the top to admit thin-walled, steel tubes. The good heat conductivity achieved by such construction makes this feature desirable in similar apparatus.⁸⁷⁻⁹¹

Schimmel¹⁰² made comparative tests on 3 German coals by the penetrometer and gas-flow test methods. The iron retort tube, size of coal charge, and rate of heating were the same in the two methods. In the penetrometer test the first sinking of the loaded needle into the coal charge was considered the softening temperature, and the end of sinking the solidification temperature. Rates of sinking were plotted against temperatures. The softening temperatures of Prosper II, Zwickau-Obenhohndorf, and Dudweiler coals were 413, 400, and 400° C, respectively; their corresponding solidification temperatures were 490, 470, and 460° C. In comparison, the gas-flow test method gave softening temperatures of 422, 400, and 398° C and solidification temperatures of 485, 470, and 475° C, respectively, for the 3 coals. In the gas-flow method, Schimmel designated the peak point of the gas pressure-temperature curve as corresponding to the solidification temperature rather than the maximum of plasticity as designated by Foxwell.¹⁰³

Pieters¹⁰⁴ determined the softening point of coal from the sinking of a 5-millimeter-diameter steel rod with pointed end into the heated sample. The vertical movement of the rod was magnified and recorded on a revolving drum as a function of temperature. Heating was carried out

at a rate of 9° C per minute. An increased rate of sinking of the rod indicated an increased fluidity of the resultant plastic mass.

Heuser¹⁰⁵ adapted the automatically controlled apparatus of Bunte and Baum for determining the melting-point curve of coal ash¹⁰⁶ (see also ref. 94) to the softening-point determination of bituminous coal. The softening curve, automatically drawn during the test, showed the displacement of the piston, or depth of sinking, in millimeters plotted as ordinates against degrees Centigrade as abscissas. The "beginning of softening" was indicated by the first slight fall in the curve; the "softening temperature" was taken as the intersection of the curve with a line drawn parallel to and 5 millimeters below the null line on the recorder strip. The steepness of fall of the curve gave a criterion for estimating the degree of plasticity of the coals tested.

Šimek and Coufalík¹⁰⁷ used the penetrometer apparatus of Heuser¹⁰⁵ to determine the softening points of the petrographic constituents clarain, durain, and fusain of a coal from the Ostrau-Karwin district. Only clarain really melted, at about 450° C and within a range of 10° C. The coal sample itself showed a melting range of 30 to 40° C.

Coufalík¹⁰⁸ modified the Heuser apparatus¹⁰⁵ in minor respects. A study of various factors showed that: (1) higher compression of the briquet increased the observed softening temperature of the coal on account of slower heat penetration into the denser charge; (2) introduction

¹⁰⁵ Heuser, P., *Glückauf*, **67**, 432-4 (1931).

¹⁰⁶ Bunte, K., and Baum, K., *Gas- u. Wasserfach*, **71**, 97-101, 125-30 (1928).

¹⁰⁷ Šimek, B. G., and Coufalík, F., *Mitt. Kohlenforsch.-Inst. Prag*, **2**, 114-24 (1935).

¹⁰⁸ Coufalík, F., *Mitt. Kohlenforsch.-Inst. Prag*, **2**, 292-307 (1935).

¹⁰² Schimmel, F., *Brennstoff-Chem.*, **10**, 319-21 (1929).

¹⁰³ Foxwell, G. E., *Fuel*, **3**, 122-8 (1924).

¹⁰⁴ Pieters, H. A. J., *Rec. trav. chim.*, **49**, IV, 289-306 (1930) (in English).

of air instead of nitrogen at the base of the coal tube caused a lowering in the characteristic temperatures and a narrowing of the plastic range, these effects being most pronounced with the larger grain size of coal and faster heating rate; and (3) weighting the needle with 300-, 500-, 550-, and 650-gram loads gave softening points of 475, 455, 442, and 433° C, respectively, for the Ostrau-Karwin coking coal heated at a rate of 10° C per 3 minutes.

Gieseler¹⁰⁹ compared results obtained with the penetrometer method with those obtained in a gas-flow (Foxwell) test on 10 coals ranging in volatile-matter content from 27.2 to 37.5 percent (pure coal basis). Additional comparative tests by these two methods were made later²⁴ on 9 Ruhr, 4 Lower Silesian, and 6 Upper Silesian coals. Temperatures of the coking mass at the solidification points obtained by the penetrometer method showed poor agreement with temperatures of maximum resistance observed in the gas-flow tests in the two investigations.

Gieseler¹¹⁰ also measured the rates of sinking of penetrometer needles with different types of points into plastic coal. He used, first, a loaded, vertically placed needle having a hemispherical point. The needle was fastened in the lower end of the rod, which was loaded by a suitable weight at the top. The needle sank only a little way into the coal and then stopped or was even raised again by the expansion pressure of the coal.

In a second apparatus identical with that just described, except that the needle was replaced by a metal ball at the bottom of the coal charge and this ball attached to a fine wire leading up over a pulley to a counterbalance just equalizing the tension on the ball, Gieseler determined the upward

movement of the ball through the coal during its softening. At the resolidification point of the coal, the movement of the ball ceased. Trouble was experienced from cementation of material on and a warping of the wire during the test.

Kaatz and Richter²⁷ studied the softening point of coals by a penetrometer method and examined the following factors: (1) density of the compressed coal; (2) form and strength of the penetrometer needle; (3) magnitude of the added load on the needle, whereby the frictional resistance of the apparatus must be also considered; (4) heating rates; and (5) methods of measuring temperature. These factors were standardized for the test method so that check results to within 1° C were claimed to be possible. The softening points of 4 German coals were reported. The softening points of a Silesian coal under loads of 500, 300, and 150 grams were observed to be 398, 406, and 415° C, respectively.

GAS-FLOW OR FOXWELL TEST METHODS

The "gas-flow" or Foxwell test method¹¹¹ (see also ref. 103) depends upon the change in resistance to flow of a stream of inert gas caused by the back pressure developed in a plug or column of heated coal. The charge is usually sized within certain limits and is often mixed with an inert material, such as electrode carbon, to increase its porosity. Consequently, the sample is not usually representative of the original coal. The charge is heated at any desired rate in either a *horizontal* or *vertical* tube through which a stream of purified and preheated inert gas (nitrogen, carbon dioxide, coke oven, or natural gas) is passed at a known pressure. Usually the tube and charge are freed of air by a pre-

¹⁰⁹ Gieseler, K., *Glückauf*, **68**, 1102-4 (1932).

¹¹⁰ Gieseler, K., *Glückauf*, **70**, 178-83 (1934).

¹¹¹ Foxwell, G. E., *J. Soc. Chem. Ind.*, **40**, 193-201T (1921).

liminary sweeping with the inert gas before the test proper is started. The resistance to gas flow offered by the heated column of coal is measured as the temperature is increased. For coking coals this resistance or pressure begins to increase when the coal starts to soften, rises to a maximum, and then usually decreases to its original value at the start of the test. The more significant data usually recorded are the maximum pressure and the temperatures of initial softening and of maximum pressure. The last has often been erroneously called the solidification temperature. In such tests, however, depending upon the coal, the solidification of the heated coal mass may take place below, at, or above the temperature corresponding to the maximum pressure.

In 1921, Foxwell¹¹¹ in his first fundamental study of the path of travel of gases in the coke oven found that the resistance to gas flow, m , namely, the pressure required to force 1 cubic centimeter (N.T.P.) of gas per minute through a 1-cubic-centimeter volume of coal, was higher for any temperature within the plastic temperature range of the coal than that expected from theoretical considerations of the laws governing the passage of gases through porous inert solids. The increments in m varied with the nature of the coal, being larger for the better coking coals. This observation led to a new experimental method for determining the values of m at various temperatures within the plastic range.

Dry coal was packed to form a column in a hard-glass tube which was then heated in a sand bath within a gas-heated furnace. Gas, presumably inert, was passed through the coal column at a controlled initial rate, no further adjustments being made during the test. Foxwell recognized that "owing to back pressure the rate of flow of gas from the holder slackened and flow ulti-

mately ceased when the back pressure was at a maximum." A temperature rise of 5° C per minute was maintained, and temperature and pressure readings were taken every 2 minutes.

Temperatures for the beginning and end of the plastic range and for maximum plasticity, defined as that temperature at which resistance to flow of gases reached a maximum, were determined for 9 coals and 1 coal blend. For a good-coking Durham coal plasticity developed at 330° C, increased between 380 and 430° C, reached a maximum at 400° C, and ended at 500° C. Poorly coking coals showed a low resistance at maximum plasticity, whereas non-coking coals, which did not fuse, offered no appreciable resistance during the test. In general, maximum plasticity was observed at lower temperatures for coals of higher volatile-matter content. Thus, the maxima appeared between 400 and 470° C for coals containing 30 percent of volatile matter [as tested], whereas these maxima were between 500 and 520° C for Welsh coals with 15 to 20 percent of volatile-matter content [as tested]. The Welsh coals also showed a second, although smaller, maximum resistance between 540 and 580° C. Foxwell explained this by saying, "Anthracitisation has resulted in the destruction of the more easily decomposable substances, or possibly in their partial destruction, the products formed having a higher decomposition point."

Foxwell¹⁰⁸ later modified his original gas-flow method¹¹¹ to eliminate certain sources of inaccuracy and to provide a more direct measure of the resistance to gas flow through coal undergoing carbonization at a continuously rising temperature. Special attention was directed to the method of packing the coal column, measurement of temperature, and control of gas pressure.

To carry out a test the gas reservoir, gas

holder, and connecting tubes were filled with gas (presumably inert) and the coal was heated at the desired rate to 300° C. At this temperature the rate of gas flow from the holder was adjusted to about 20 cubic centimeters per minute at zero gage pressure and 3,500 millimeters water head. Readings of temperatures, pressures, and volumes of gas in the gas holder were taken every t minutes, that is, every 10° C over the temperature range 330 to 540° C.

Foxwell calculated the pressure m required to force 1 cubic centimeter (N.T.P.) of gas per minute through a cubic centimeter of the material maintained at T° C from the expression

$$m = \frac{p \times s}{v \times l}$$

where p is the gage pressure in millimeters of water; s is the cross section of the tube in square centimeters; v is the total volume of gas, in cubic centimeters, passing through the coal per minute; and l is the length of the coal column in centimeters.

The relationship between the value of m and temperature determined the "plastic curve." The general characteristic of this curve showed that m increased at a uniform rate up to about 400° C and beyond this became higher than demanded by theory; this deviation became still greater at higher temperatures, until a maximum value of m was reached. Thereafter, the value of m remained virtually constant for some time or dropped rapidly to a "low point," then continued falling to 900° C, after which it might rise again. The mean values of m for coke from one coal were found to be 0.410 millimeter between 550 and 700° C and 0.062 millimeter between 700 and 950° C.

It appears to the writer that these values are of such small magnitude that the experimental errors would make them of

questionable value in any quantitative interpretations of the plastic properties of the coals studied.

In 1925, Layng and Hathorne¹¹² stated, "In 1921 at the Pittsburgh meeting of the American Chemical Society, the authors gave notice and some data of their work on American coals using a somewhat similar method" to that of Foxwell.¹¹¹ The "work" referred to was evidently Paper 19, "The Softening Point of Coal—Its Determination and Significance," by T. E. Layng, W. S. Hathorne, A. W. Coffman, and S. W. Parr, which was presented before the Section of Gas and Fuel Chemistry of the American Chemical Society at its meeting in September, 1922, instead of in 1921, and was reviewed in *Chemical and Metallurgical Engineering*, 27, 648-649 (1922). Layng and Hathorne apparently were not aware of the 1924 publication of Foxwell.¹⁰³

The apparatus described by Layng and Hathorne consisted essentially of an accurately controlled, *vertical*, electric tube furnace, a constant-head device for supplying nitrogen gas to the tube containing the coal, a manometer for measuring the pressure developed, and a pyrometer for measuring the temperature outside the coal tube. Readings of time, temperature, and pressure were made and recorded every 3 to 5 minutes until the coal had passed through its critical stage and the pressure of the nitrogen gas stream was again constant.

Forty-two American coals, which included 25 Illinois bituminous, 11 Eastern bituminous, and 6 semibituminous coals, were tested. The softening temperature (initial plasticity) checked within 1 to 2° C, and the temperature of maximum pressure (initial solidification) within

¹¹² Layng, T. E., and Hathorne, W. S., *Ind. Eng. Chem.*, 17, 165-7 (1925).

10° C. The maximum pressure in millimeters water gage, the temperature of coke formation in degrees Centigrade, and the length of coke in centimeters also were reported. The younger (Illinois) coals became plastic at lower temperatures than the higher-rank coals, but too few of the latter were tested to determine whether the relation was completely general.

Foxwell,¹¹³ calling attention to the neglect of Layng and Hathorne¹¹² in not citing his own recent investigation,¹⁰³ stated that both his earlier work¹¹¹ and the work of Layng and Hathorne¹¹² were open to several objections. Layng and Hathorne did not state at what rate the temperature of the coal was increased. The rate of increase would have little influence upon the temperature at which plasticity begins but would affect greatly the temperature of maximum pressure, the extent of the plastic range, and the pressure developed. Examples of 3 typical English coking coals using 1, 3, and 5° C per minute rates of heating were given. Foxwell stated that there is "no definite temperature of completion of the plastic stage; the coke continues to drop slightly in resistance for as much as 200 or 300° C." Layng and Hathorne took no precaution to prevent the coal from expanding, thus allowing the resistance to be lowered.

A later apparatus¹¹⁴ with improved construction features had a small gas space, so that the pressure change registered by the gages corresponded very quickly to the resistance of the coal.

Layng and Coffman¹¹⁵ used the method of Layng and Hathorne to determine the plastic properties of fresh, weathered, oxidized, and preheated coals. All samples

were first ground to a size between 20- and 60-mesh, and the heating rate was 2° C per minute in all determinations. Temperatures of initial plasticity, maximum pressure, and coke formation, the maximum pressure in millimeters water gage, and the resulting coke quality were determined on each of 9 fresh coals and 2 weathered samples. The fresh coals included 5 from Illinois, 2 from Kentucky, and 1 each from West Virginia and Pennsylvania. The 2 weathered samples of an Illinois coal had been in storage for 6 weeks. One was from the outside of the storage pile, the other from a point in the pile where localized heating had led to spontaneous combustion.

Of the 2 weathered coals the sample from the outside of the pile showed less change in plastic properties than the other sample. Similar data were obtained on 2 of the Illinois coals, on 1 of the Kentucky coals, and on the West Virginia and Pennsylvania coals after they had been subjected to accelerated oxidation with oxygen in a constant temperature oven at 110° C for various periods of time up to 300 hours. With accelerated oxidation, the data, compared with those obtained on the original fresh samples, showed: (1) increases in the temperature of initial plasticity; (2) decreases in the maximum pressure; (3) decreases in the temperature of solid coke formation; and (4) progressive decreases in the quality of coke. The coals with the greatest plastic range oxidized less easily and could be stored with less difficulty.

The other 4 fresh coals (3 from Illinois and 1 from Kentucky) were preheated in either air or nitrogen to temperatures of 150, 200, 250, 300, or 350° C, and then cooled in the same atmosphere. The plastic properties were determined and compared with similar data on the fresh coal.

Preheating increased the temperature of

¹¹³ Foxwell, G. E., *Ind. Eng. Chem.*, **17**, 1161 (1925).

¹¹⁴ Foxwell, G. E., *Fuel*, **11**, 4-19 (1932).

¹¹⁵ Layng, T. E., and Coffman, A. W., *Ind. Eng. Chem.*, **19**, 924-5 (1927).

initial plasticity. With increasingly higher temperature of preheating in air the maximum pressure was decreased, but it remained the same or was decreased in a nitrogen atmosphere. In nitrogen, one coal showed first an increase and then a decrease in maximum pressure. The authors stated that the Kentucky (Jellico County) coal gave an even better coke, after preheating in air at 150° C, than was obtained directly from the fresh coal itself, whereas the coke from preheated Saline County Illinois coal was not improved in quality by the preheat treatment. The authors did not state how coke quality was determined. The temperature of 150° C appeared to be the maximum to which a coal could be preheated in air without affecting its coke quality. Preheating to higher temperatures in a nitrogen atmosphere did not affect the coke quality.

The results indicated that they should offer promise: (1) in aiding in the classification of coals that soften on heating; (2) in tracing any particular seam of coal; (3) in establishing the particular state of any coal that has been weathered; and (4) in determining the effect of conditioning on coal.

Coffman and Layng¹¹⁶ modified the Layng and Hathorne test method in several respects. The importance of maintaining the same rate of temperature increase in comparative tests was emphasized so as to avoid variations in observed temperatures of initial plasticity and solidification. Temperatures outside the coal tube at the middle height of the coal sample were measured by a standard Hoskins indicator and base-metal thermocouple. Time, temperature, and pressure readings were made and recorded at 2-minute intervals. The object of the investigation was to show the

application of the test in evaluating the so-called agglutinating power of any coal and also to establish that the agglutinating value is the resultant of a large number of governing factors, chief of which are rate of carbonization, previous conditioning, amount of weathering, the chemical reactions between the constituents of the coal.

The authors concluded that the "temperature of coke formation" was relatively unimportant because it merely marked the end of a very rapid falling off in pressure; they emphasized that the point of maximum pressure really marked the completion of the complex processes, chiefly indicated by softening and by cell formation. This cell formation, which is the result of all the reactions taking place, ended in fixation of the coal mass and explained the rapid diminution of pressure. They also concluded that the important portion of the temperature-pressure curve representing the true range of plasticity lay between the initial softening temperature and point of maximum pressure.

A graphical study on this portion of the curve led to the development of an expression which they called the "differential index" or "agglutinating index." This index was derived solely from pressure-time relations between the initial softening point and the point of maximum pressure. The time rate of increase in pressure was calculated at regular intervals and plotted against time. The curves showed that the value of dp/dt increased with time to a maximum and then decreased. *The maximum value of dp/dt for any differential softening curve was called the "differential index" or "agglutinating index" of the coal.*

With one or two exceptions, the values of the "differential index" for 26 American coals, determined at rates of heating between 1 and 2° C per minute, arranged themselves in a natural order according to

¹¹⁶ Coffman, A. W., and Layng, T. E., *Ind. Eng. Chem.*, **20**, 165-70 (1928).

the properties of the coals. At higher heating rates more exceptions were observed. The author suggested that softening coals may be classified as follows: Illinois bituminous, index 20-40; semibituminous, 30-40; and Eastern bituminous, 50-125.

The dp/dt values plotted as ordinates against time in minutes as abscissas gave curves of the form of Maxwell distribution curves, thus indicating the manner in which the energy in a coal is proportioned over the plastic range. For each of the 19 coals for which data were plotted in this way the energy was distributed in a different manner, but coals of the same type showed approximately equal total quantities of energy, as represented by the areas beneath their curves. From these curves it appeared that for a coal to form a coke two conditions must be fulfilled: (1) the differential index must have a value above 20; and (2) the total energy must be used in a comparatively short time, giving rise to a peak in the curve. By varying four factors governing agglutinating value it appeared that poorly coking coals might also fulfill these conditions. Special studies were made, therefore, of the effect of the following four factors.

Effect of the Rate of Heating. The method used was the same as described, except that no nitrogen gas was passed in during the test. It was believed that in this way only the pressure of the liberated gases would correspond more nearly to conditions for measuring the true energy index of the coal. The data obtained without nitrogen gas were comparable to one another for the different rates of heating, and they checked the method using nitrogen gas as to softening and solidification temperatures but gave higher dp/dt values. It was shown that an increased rate of

heating increased the value of dp/dt to an appreciable degree.

Conditioning Treatment. The data of Layng and Coffman¹¹⁵ showing the effect of preheating in various atmospheres were calculated in terms of dp/dt values. The effect of pretreatment showed that the dp/dt values were changed greatly. There did not seem to be any regularity between the results obtained by Layng and Coffman and the dp/dt values, except, perhaps, that the poorer the quality of coke the lower the dp/dt values become, although there were several striking exceptions to this relationship.

Weathering. The data of Layng and Coffman showing the effect of accelerated oxidation on the plastic properties of the 5 coals tested also were calculated in terms of dp/dt values. In general, the dp/dt values decreased with the extent of oxidation (amount of weathering), showing that the coking energy and agglutinating values of the coals were decreased by this treatment.

Chemical Interactions. The chemical changes depended upon the other three factors just discussed.

Marquard¹¹⁷ determined the plastic properties of 5 American coals by the gas-flow method; a description of apparatus and procedure was not given. The coals included a low-volatile Pocahontas and 4 high-volatile A coals, Freeport, Palmer, Colonial, and Filbert. These 4 coals had nearly the same volatile-matter content but gave different "melting" temperatures and relatively different emissions of gases during their plastic state. Except for the higher maximum pressure of the Filbert coal, the maxima were around 4.4 inches water gage. The "melting" points were

¹¹⁷ Marquard, F. F., *Yearbook Am. Iron Steel Inst.*, **18**, 83-112 (1928); *Blast Furnace Steel Plant*, **16**, 754-7, 914-6 (1928).

indicated by the initial sharp increases in pressure, and all corresponded to around 0.8 to 0.9 inch water gage. None of the 5 coals showed a zero pressure at 500° C, the end of the test, but pressure of 1.2 inches or more water gage. The relative quantities of gases evolved during the plastic state, indicated by the relative areas under the plastic curves, agreed well with the proportions of volatile matter expelled during the tests, as determined from the coal samples before and after test.

The Pocahontas coal lost about half of its volatile matter, gave the highest melting temperature, and produced an inferior coke. Of the 4 coals of similar volatile-matter content, Freeport coal showed the greatest loss in volatile matter, the lowest melting temperature, and the poorest residual coke. Filbert coal showed the next greatest loss in volatile matter and the highest melting temperature, and gave a good coke. Palmer and Colonial coals gave lower losses in volatile matter, intermediate melting points, and good cokes. Filbert coal, when blended with other coals of the same melting point or gasification loss, gave good coke; with blends of different melting characteristics the coke structure was poor. Removal of slate from Palmer coal lowered the melting point approximately 50° C.

Schimmel¹⁰² made comparative measurements using the gas-flow method of Layng and Hathorne,¹¹² and the penetrometer method of Agde and Lyncker.⁹² The apparatus and procedures were modified slightly in both methods. The melting points of 3 German coals obtained by the two methods agreed closely. The temperatures of maximum pressure in the gas-flow method agreed with those of the end of the plastic range in the penetrometer method. The highest point in the Foxwell plasticity curve, therefore, must be inter-

preted as the setting point or solidification of the plastic mass and not the temperature of maximum plasticity, as Foxwell¹⁰³ had assumed.

Ball and Curtis,¹⁸ after first using the Foxwell¹⁰³ and Layng and Hathorne¹¹² gas-flow methods, developed a modified gas-flow method which provided pure dry nitrogen gas and insured accurate temperature measurements in the coal. The softening temperatures obtained by the gas-flow method were compared with the distortion temperatures of individual particles of the same coals obtained by direct visual observation in the apparatus described on page 171. The gas-flow method gave softening temperatures up to 150° C higher than those directly observed by the microfusion method. However, when briquets were substituted for individual particles of coal in the microfusion method, distortions occurred at only 15 to 20° C higher for the same coal.

Lloyd¹¹⁸ believed that high pressures, such as those developed in the procedures of Foxwell and of Layng and coworkers, were not desirable in the gas-flow method. Accordingly, he maintained a virtually constant water-gage pressure of about 1.5 inches at the start of the plastic range and never above 2.2 inches maximum for the 10 American coals studied.

Believing that the gas flow was proportional to the pressure, Lloyd calculated the gas-flow values per inch of water pressure and plotted them as ordinates against observed degrees Fahrenheit as abscissas. The resulting curves showed no sharp maxima, contrary to the sharp maximum observed and interpreted by earlier workers as a mere point function of temperature, but instead a maximum plasticity extending over a long range of tempera-

¹¹⁸ Lloyd, T. C., *Chem. & Met. Eng.*, **37**, 169-71 (1930).

ture—at least 55° C for good coking coals. Three Pennsylvania and two Kentucky high-volatile coals gave curves that were roughly symmetrical about their minimum pressure values in the temperature range of 400 to 450° C. On the other hand, curves for West Virginia low-volatile coals had sharp slopes approaching the minimum pressures around 450 to 475° C and very gradual slopes away from the minima with increased coking temperatures. The final portions of these curves, around 475 to 575° C, were nearly horizontal for the highest-grade, low-volatile, coking coals; increasing slope was considered an indication of diminishing coking power.

Plasticity tests on blends of 85 percent of high-volatile coal (Royal mine, Fayette Co., Pa.) and 15 percent of different size fractions of low-volatile coal (Carswell mine, McDowell Co., W. Va.) were compared with results of box tests made in a coke oven. Proximate analyses of the different size fractions showed but little differences, but tumbler tests on the resultant cokes from different blends showed that coke quality fell with coarser sizes of low-volatile coal used. Plastic curves on the various blends also were different.

Lloyd recommended that for good results in blending one should use two coals that enter the plastic stage at different temperatures. The coal of lower softening temperature would then near the coking stage when the other coal became liquid. Such a choice permits only one of the component coals to be in a liquid state at one time, leaving this liquid free to flow around the solid particles of the other component and thereby produce better mixing. On the other hand, if two thick, semiliquid masses are present at the same time, intermingling probably would take place more slowly owing to their mutual viscosity and resistance characteristics.

Schroth¹¹⁹ tested 6 German coals by a modification of the Layng and Hathorne method. The maximum resistances ranged from 41 to 852 millimeters water-gage pressure and increased with increasing values of the Kattwinkel caking index. The temperatures of softening were not consistent with the order of these indexes.

Swietoslowski, Roga, and Chorazy¹²⁰ modified the Layng and Hathorne test method for the determination of the plastic properties of several types of bituminous coals. The modifications introduced were not described. The determinations included: 2 Pas-de-Calais (French) and 1 Ruhr (German) semibituminous coals; 3 Ruhr, 1 Pas-de-Calais, and 1 Durham (English) low-volatile coals; 1 Pas-de-Calais, and 1 Upper Silesian (German) coking gas coals; and 1 Ruhr and 2 Northumberland (English) caking, long-flame, gas coals. A heating rate of 5° C per minute was used in all tests. The plasticity curves obtained were characteristic of each group of coals. The order of magnitude of "maximum plasticity," expressed in millimeters of water pressure for the four groups of coals, was as follows: 1 to 10 for the semibituminous; 123 to 171 for the low-volatile coking; 136 to 144 for the caking gas; and 4 to 26 for the caking, long-flame, gas coals. The temperature of "maximum plasticity" decreased with increase in the volatile content of the coal.

These authors found that briquets of satisfactory mechanical strength could be made from coking-coal slack by using a pressure of the same order as was then used in the industrial production of briquets from coal slack and pitch and by heating under one of the following condi-

¹¹⁹ Schroth, W., *Gas- u. Wasserfach*, **73**, Special No., 18-26 (May, 1930); **73**, 546-9 (1930).

¹²⁰ Swietoslowski, W., Roga, B., and Chorazy, M., *Fuel*, **9**, 421-39 (1930).

tions: (1) by heating to the temperature of incipient plasticity; (2) by prolonged heating at 390 to 440° C, temperatures at which plasticity is fully developed, to destroy partly the excess of bituminous substances; and (3) by heating at about 450° C, corresponding to the last stages of the plastic state. In the last instance the required period of heating was much reduced.

The Foxwell¹⁰³ apparatus was modified by Davidson.¹²¹ The essential difference was the introduction of a differential gage, by means of which the rate of nitrogen flow through the system could be determined at any given temperature. Heating was carried out rapidly to 250° C. The nitrogen flow was then started and the rate of heating adjusted, as desired, to 1, 3, or 5° C per minute. The pressure in the system and the rate of flow of nitrogen were noted at 5° C intervals. The change of coal to the plastic state was accompanied by an increased pressure of the system and a decrease in the rate of flow of nitrogen through the coal. When the pressure had increased to 12 cm of mercury, the flow of water into the nitrogen holder was cut off. The end of the plastic range was indicated by a sudden drop of pressure in the system.

With some coals, during part of the test, the tube became completely blocked and no nitrogen passed through the coal; some of the gas evolved from the coal passed backward into the nitrogen holder, as indicated by a negative reading on the differential gage. With poorly caking coals, when heated at the slow rate of 1° C per minute, no gas flowed back into the nitrogen holder.

Each of 12 coals from Scotland and England was tested at rates of heating of 1, 3, and 5° C per minute. The temperature of the beginning of the plastic range was

found to be independent of the rate of heating, whereas that at the end of the plastic range was raised with increased rate of heating. The maximum pressures increased with higher rates of heating. The data were correlated with the amounts of volatile matter evolved from the coals before, during, and after their plastic ranges, and also with their Gray-Campredon caking indexes. Blending experiments showed that, if the volatile matter retained by the coal at the end of the plastic range could be reduced, a coke having fewer fissures would be obtained. This was accomplished either by blending the coal with a material of low-volatile content, such as high-temperature coke, or by the addition of a coal having a higher temperature for the end of the plastic range and a lower volatile content at this temperature.

Lambris⁹⁹ used the Foxwell test method in a comparative study of the effect of three methods of pretreatment upon the expansion pressure, degree of swelling, and agglutinating number of 4 coking coals. The three pretreatments were: (1) 3 months' storage of the coal samples in stoppered glass vessels from which the air had not previously been excluded entirely; (2) preheating of the coals at 200° C in an atmosphere of nitrogen until complete loss of the expansion pressure was effected; and (3) extended treatment according to treatment 2 to cause complete loss of swelling power. The 4 coals had previously been tested in the fresh state and under condition (1) for their softening points,⁹² expansion pressure,³ degree of swelling,⁵¹ and agglutinating number.¹²² Foxwell curves were not determined on the fresh coals. The stepwise degradation of coal properties was effected progressively by pretreatments 1, 2, 3.

¹²¹ Davidson, W., *Fuel*, **9**, 489-92 (1930); *Foundry Trade J.*, **51**, 61-5 (July 26, 1934).

¹²² Meurice, A. A., *Chaleur et ind.*, **4**, 45-52 (July 1923); *Fuel*, **2**, 305-8 (1923).

With treatment 1, the coals, after storage for 3 months, still showed expanding, swelling, and caking properties. The temperatures of "highest plasticity" of the 4 coals fell within the temperature range of 490 to 515° C and were in good agreement with "softening temperatures" within the range 490 to 510° C for the same 4 coals, as determined by the penetrometer method. The penetrometer method gave softening temperatures within the range of 415 to 425° C on the fresh coals, showing that storage for 3 months had markedly raised the softening temperature.

With treatment 2, except for the coal of highest volatile content (26 percent, pure coal basis), the coals were no longer expanding; that is, the Foxwell curves were straight lines. The exceptional coal still showed 22.3 percent by volume "degree of swelling" and also caking properties. With treatment 3 all Foxwell curves were straight lines, showing that plasticity had been destroyed completely; only caking properties were still present.

It was concluded that, by the stepwise pretreatments above described, the softening point, expansion pressure, degree of swelling, and agglutinating value could be destroyed in the order named, one by one, without materially affecting the properties following in this series.

Schläpfer and Müller⁸⁸ used a slightly modified Layng-Hathorne apparatus. Gas permeability curves (millimeters water pressure as ordinates plotted versus temperatures in degrees Centigrade as abscissas) were determined at both rapid and slow rates of heating for 4 coals: Boltigen (Bern gas and coking coal, 86.3 percent dry, ash-free carbon); Neumühl (Ruhr fat coal, 89.1 percent dry, ash-free carbon); Heinitz (Saar fat coal, 85.9 percent dry, ash-free carbon); and La Houve (Saar flame coal, 81.3 percent dry, ash-free carbon).

With rapid heating the coking was ended at 600° C in 20 minutes. Softening temperatures between 350 and 400° C were observed, after which the gas pressures rose rapidly to their maxima and then fell rapidly to low values. The Boltigen coal showed the highest resistance, about 568 millimeters water gage, contrary to what might be expected from the weak coke produced from this coal. The authors explained this as due to the formation of a tough film, caused by agglutination of the non-melted portions with the melted bitumen, which then by progressive decomposition formed a brittle and friable coke. The noncaking La Houve coal, on the contrary, gave a maximum resistance of only 138 millimeters water-gage pressure on account of the very small cementation of the particles and, therefore, small resistance to gas flow. The Neumühl and Heinitz coals showed intermediate resistances of 500 and 244 millimeters water gage, respectively.

Slow heating, up to 550° C in 2 hours, reduced the plasticity. Neumühl coal alone preserved a real degree of cementation, showing a resistance of 200 millimeters water-gage pressure. Boltigen coal no longer gave the same cementation, showing a resistance of only 138 millimeters water-gage pressure. Heinitz and La Houve coals, each with resistances of 75 millimeters water-gage pressure, scarcely coked, and most of the residue could be shaken out as powder at the end of the tests.

Gas permeability curves were determined at the slow heating rate on the 4 coals after preheating. All coals showed higher initial softening temperatures and lower maximum pressures by this pretreatment.

The results obtained by the gas-flow method were compared with those found by the authors on the same coals with their dilatometer method. The swelling curves

plotted from the results of the dilatometer method showed that the temperatures for the end of swelling coincided with those for maximum resistance in the gas-flow curves. It was concluded that the maximum resistance temperatures in the gas-flow test were not the points of maximum plasticity, as Foxwell had believed, but those of solid coke formation. This conclusion was in agreement with similar measurements made by Schimmel.¹⁰²

Schläpfer and Müller concluded that a correct picture of the actual processes taking place during coking could not be given from gas-permeability measurements. They advocated the use of either the wire sling penetrometer method of Greger⁹⁸ or the penetrometer method of Agde and Lyncker.⁹²

Some 250 tests were made by the U. S. Bureau of Mines laboratory^{87, 88, 89, 90} with two modifications of the Layng and Hathorne method. Plastic-range curves were constructed by plotting pressures in millimeters water gage as ordinates against temperatures in degrees Centigrade as abscissas. Characteristic points on the curve were the initial softening temperature at which the pressure first starts to increase, the solidification temperature, or the temperature of maximum pressure, and the maximum pressure. The values of maximum pressure (resistances to gas flow) were not closely duplicable, and the temperature-pressure relationships were not sharply defined. As the method furnished but little reliable information that could not be more accurately and completely provided by other methods it was discontinued as impracticable.

Pieters¹²³ used a gas-flow method to test 3 coals. The method provided useful information for making satisfactory briquets

from coals of various mesh sizes and different amounts of ordinary and oxidized tars.

Roga¹²⁴ used a modification of the Foxwell method. Increased rates of nitrogen flow gave higher maxima for the plasticity curves. The shape of the curves was affected also by the use of coal of different grain sizes, especially with the finer sizes. Plasticity increased with rate of heating owing to the melting of bituminous substances preceding their decomposition. For coking coals the plastic state was observed without exception but was not developed in all gas- and gas-flaming coals.

Damm and Korten¹²⁵ used Foxwell curves to establish the temperature limits of the preheating (degasification) and plastic (degasification during fusion) zones of degasification.

Chorazy³⁰ correlated the results of plasticity tests obtained by a modification of the Foxwell method with results of pyridine absorption tests. Plasticity of the coals was developed at temperatures similar to those at which pyridine-vapor absorption was enhanced. The changes taking place before and during the plastic stage could be evaluated from the amount of pyridine vapor absorbed by previously heated coals.

Chorazy¹²⁶ also determined the plastic properties of 7 Polish coals. Three of the coals were noncoking and exhibited no plasticity. For 4 Polish coals, whose permanganate reactivity indexes were 61 or less, the shape of their Foxwell curves showed a regular dependence of the plastic property of the coal on its content of hydrocarbons and resins; the higher the maximum resistance, or maximum pressure,

¹²⁴ Roga, B., *Przemysl Chem.*, **15**, 305-13 (1931).

¹²⁵ Damm, P., and Korten, F., *Glückauf*, **67**, 1339-45 (1931).

¹²⁶ Chorazy, M., *Fuel*, **13**, 294-9 (1934).

¹²³ Pieters, H. A. J., *Rec. trav. chim.*, **50**, 860-4 (1931); *Fuel*, **10**, 443-5 (1931).

point on the curve, the higher was the hydrocarbon and resin content.

Hofmeister¹²⁷ used a simplified Foxwell apparatus to determine the plastic range of 7 German coking coals of known ash and volatile-matter content. The effect of the rate and manner of heating received special study. Increasing the heating rate from 1–4 to 10° C per minute shifted the characteristic temperatures and the maximum pressures to higher values. Lower heating rates, such as 1° C per minute, were recommended. Sudden heating of the coal during the period of the rising portion of the temperature-pressure curve gave a residue, which was caked uniformly on the edges, but only feebly sintered, and even partly granular, on the inside. The maximum pressure on the curve, therefore, indicated only the point of smallest gas permeability and permitted no conclusion to be made about the temperature of resolidification of the coal mass. The results were correlated with data obtained for caking numbers, expansion pressures, and pre-, during-, and after-degasification determinations as functions of the temperatures to which the coals were heated. The coking coals were characterized from these data as to their relative coking properties.

Gieseler¹⁰⁹ modified the Layng and Hathorne test method so that the coal was heated uniformly and its temperature measured accurately. He agreed with Hofmeister on the effect of sudden heating during the period of the rising portion of the temperature-pressure curve, on the resolidification temperature of the coal, and on the nature of the caked residue. Proof of this was offered in the fact that, whereas the 10 coals tested showed excellent agreement between their softening point values, as determined by the gas-flow method and

the Schimmel penetrometer method, 4 of the 10 coals gave resolidification temperatures that were 22 to 32° C lower by the gas-flow test. In these coals, even in the temperature region in which the pressure was already decreasing, that is, after the "maximum pressure" had been observed, the charge was still strongly swollen, very plastic, and frothy. The pressure decrease, therefore, had set in before solidification of the coal had taken place. One must conclude, therefore, that the earlier interpretations of the Foxwell curves of such coals, which defined the plastic range from the softening to the maximum pressure points, giving a softening zone of only about 50° C, were incorrect.

Further modifications of the gas-flow test method were also made by Gieseler,²⁴ so that it was possible to determine the gas flow-temperature relations as well as to observe visually what was occurring during the test, especially whether the coal sintered, caked, and swelled. The temperatures of softening and resolidification of 9 Ruhr, 4 Lower Silesian, and 6 Upper Silesian coals were determined both by this gas-flow and by the Schimmel penetrometer test method. The degree of swelling was determined also by the latter method on the same coals. The volatile-matter content of the coals from the three sources ranged from 17.3 to 26.0, 24.7 to 34.8, and 29.6 to 36.3 percent (pure-coal basis), respectively. The temperatures of the beginning and of the end of swelling were observed, and the ratio of the volume of semicoke formed to that of the original coal charge was determined.

The degree of swelling for the Ruhr coals increased regularly with the increase in their volatile content and their softening zone as determined by the penetrometer method; this regularity did not hold with the Lower and Upper Silesian coal

¹²⁷ Hofmeister, B., *Glückauf*, **68**, 405–11 (1932).

samples. Foxwell (temperature-pressure) curves were constructed for 3 coals from each district, and the corresponding temperatures of softening and resolidification found by the penetrometer method were marked on the appropriate curves. Softening temperatures by the two methods showed fair agreement, but the resolidification temperatures by the penetrometer method were sometimes below, sometimes at, and sometimes above the temperatures corresponding to maximum pressures on the Foxwell curves. Comparative measurements of temperatures by the penetrometer method made at the center of the coal pellet and in the outside salt bath showed that the greatest difference over a temperature range from about 320 to above 550° C was within 3° C for each of the 4 coals tested.

Ping¹²⁸ used a slightly modified Layng and Hathorne apparatus. Seventeen Chinese coals were tested for their fusion point, solidification point, pressure at fusion point, pressure at solidification point, and swelling coefficient (length of coke divided by length of coal). Seven of the coals also showed an "initial softening point," defined as the temperature corresponding to a sudden reduction in pressure after the moisture had been expelled from the charge. Ratios of the pressure differences (between solidification and fusion points) to the plastic temperature ranges, designated as P.D./P.R. ratios, did not show any consistent relationships with the rank or other properties of the coals.

Davies and Mott⁸² used an apparatus almost identical with that of Foxwell. The calculation of m by Foxwell was criticized because his coal charge was free to expand. Davies and Mott kept their coal charge at

a constant volume and plotted pressures directly against temperatures. The maximum resistance tended to decrease with decreased carbon content of the 13 English coking coals tested.

Agde and Winter¹²⁹ used the Foxwell method to determine the effect of oxidation by air in certain temperature zones of softening and rehardening of 4 Westphalian coals. The coals were oxidized at 100° C for various periods of time up to 300 hours. This pretreatment caused the softening temperatures of 2 coals to be raised, but produced no change in the other 2. The height (maximum resistance) of all Foxwell curves was reduced, and the hardening or setting point was increased in all 4 coals. The quality of coke from the oxidized coals was poor. The theory of Lambris⁹⁹ on the effect of oxidation upon plastic properties was confirmed in part, whereas theories of Foxwell¹⁰³ and of Layng and Coffman¹¹⁵ were refuted.

Coufalík¹⁰⁸ used a modified Foxwell procedure to study the influence of certain factors. It was found that grain sizes of coal, 0.1, 0.25, 0.50, and 1 millimeter, gave the same plastic temperature ranges but higher maximum resistances with increase in size of coal. Rates of gas flow between 40 and 75 cubic centimeters per minute did not affect appreciably the plastic temperature range, but increased rate of flow raised the values of maximum resistances. A rate of 40 to 60 cubic centimeters per minute was proposed as standard. Rates of heating of 10° C per 3 minutes, 10° C per minute, and 20° C per minute gave higher maximum resistances, respectively, but did not change the plastic temperature range. Fresh samples and thorough mixing, to insure the same proportions of petrographic

¹²⁸ Ping, K., *Bull. Geol. Survey China* **21**, 45-56 (1933); *Contrib. Sin. Yuan Fuel Lab., Geol. Survey China*, **10** (July, 1933), 14 pp.

¹²⁹ Agde, G., and Winter, A., *Brennstoff-Chem.*, **15**, 64-7 (1934).

constituents in duplicate samples, were recommended.

Bunte¹³⁰ determined the "softening behavior" or resistance to gas flow by the Foxwell method. The study included Heinitz, Radbod, Hannover Hannibal, Bonifatius, Eschweiler, Hohenzollern, and Gleiwitz fresh coals; the bright, dull, and fibrous fresh portions of the typical Heinitz gas coal; its bright portion after 1 and 3 months' storage; Eschweiler expanding and Gleiwitz coking coals after the same periods of storage; and several different blends each of Eschweiler and Hohenzollern and of Heinitz and Leopold coals and a 50 : 50 blend of Hannover Hannibal and Hugo coals. Coals of 0.5- to 1.0-millimeter grain size, a nitrogen flow of 50 cubic centimeters per minute, and a heating rate of 1° C per minute were used.

The first 4 coals showed decreasing maximum resistances to gas flow in the order named, which is also the order of decreasing geological age of these coals. This was to be expected on account of polymerization of the bitumens. The data obtained were plotted in the usual way, that is, resistance to gas flow in millimeters water-gage versus degrees Centigrade, as well as in dp/dt (change of pressure with time) curves. The rising portion of the dp/dt curve was designated the "liquefaction velocity" curve. A low liquefaction velocity, corresponding to a steep curve, and a rapid resolidification followed by a steep descending dp/dt curve were requisite for good coke formation.

Foxwell curves for the bright, dull, and fibrous portions of the typical Heinitz gas coal and for the fresh coal as a whole showed that the curve for the fresh coal lay between the proportionally higher curve for the bright and the lower curve for the

dull coal. The fibrous coal did not melt and showed no resistance. Storage of the bright coal for 1 and 3 months reduced plasticity in that order. Similar effects were produced on the expanding Eschweiler and Gleiwitz coking coals after storage for the same periods. The former was changed greatly with storage, the latter very little. The effects produced by storage correlated well with the relative rates of oxygen absorption for the different types of coal.

Resistances to gas flow were determined for 75 : 25, 65 : 35, 50 : 50, and 25 : 75 blends of Eschweiler and Hohenzollern coals, respectively, for 75 : 25, 50 : 50, and 25 : 75 blends of Heinitz and Leopold coals, and for a 50 : 50 blend of Hannover Hannibal and Hugo coals. The "softening behavior" (Foxwell) curves and the "liquefaction velocity" curves showed that the effect of blending two coals cannot be established entirely from the curves of the blended constituents. Coke yields also were greater than predicted from the properties of each constituent.

Yields of gas at temperatures up to 500° C and the volumetric and gravimetric rates of change of gas evolution were determined for a number of coals. Because of polymerization of the bitumen, the evolution of gas occurred at higher temperatures with the increasing geological age of the coals. Comparison of these results with Foxwell and dp/dt curves showed the value of laboratory tests in relation to expected behavior of the coals and blends in coke-plant practice.

Bunte and Löhr¹³¹ made a critical study of the gas-flow test apparatus and procedure and of the effects of various pretreatments (sizing, aging, preheating, and blending) of the coal sample on the test results.

¹³⁰ Bunte, K., *Gas- u. Wasserfach*, **76**, 685-93 (1933).

¹³¹ Bunte, K., and Löhr, H., *Gas- u. Wasserfach*, **77**, 242-7, 261-9 (1934).

Twenty-six coals, mostly from the Ruhr district, ranging in volatile-matter content from 14.4 to 42 percent (pure-coal basis), were studied. Nine series of blends, 18 in all, containing different proportions of two different coals, also were investigated. Reproducibility of duplicate measurements on the same coal was good, except for the maximum resistance values, for which the differences were attributed to variations in proportions of petrographic constituents in individual samples. Checks of 0 to 3° C for the "semicoke point" were claimed.

Proximate analyses and crucible tests were carried out on the 26 individual coals and correlated with the data of the gas-flow tests. Coals containing less than 15 percent volatile matter did not fuse. Coking coals containing 15 to 18 percent volatile showed high softening and semicoke temperatures. Coals with a volatile content above 18 percent had softening points under 400° C and higher "semicoke" points, and, consequently, gave broader melting zones. The relationship between the content of volatile matter and the height of the maximum resistance was very irregular. The caking qualities were estimated much better from Bochum crucible test results than from the volatile-matter contents of the coals.

Sixteen blends, each consisting of 2 coals of different swelling and caking properties and blended in various proportions, were tested by the gas-flow method. The results of these tests were compared with those of the individual coals used in blending. The usual method of plotting the test data gave curves which were difficult to interpret. A better method of evaluation was found in the dp/dt curves. The maximum value of dp/dt defined the point of maximum plasticity. The corresponding temperature lay between the softening and semicoke temperature points; thus, the ascending por-

tion of the usual gas-flow curve could be divided into two temperature segments which could be so related to each other as to offer a better explanation of the melting ability of coal blends.

The plastic behavior of a coal blend could not be predicted from that of the individual constituent coals. Significant points to be noted in the dp/dt curve were the temperature range in which the coke is a fused mass, the speed with which the penetration of gas decreases, and the rate of change of viscosity (slope of the curve) before and after the maximum. The dp/dt curve should rise slowly within a range of 40 to 50° C and then fall rapidly. For a satisfactory coke a maximum resistance between 100 and 200 millimeters water gage was recommended.

Bunte, Brückner, and Ludewig¹³² devised an apparatus in which softening behavior, degree of swelling, and volumetric and gravimetric yields of gas evolved from a coal could be studied simultaneously under like conditions of heating. Tests were made on 7 German coals. These included a Ruhr gas flame coal, an Upper Silesian gas flame coal, an Upper Silesian coal dust, a Saar gas coal, an Upper Silesian coking coal, a coking coal from the Wurm district, and a Ruhr lean coal. They contained 35.6, 32.9, 31.2, 32.9, 28.1, 17.9, and 12.6 percent of volatile matter (air-dry basis), respectively. Only the Saar gas coal and the two coking coals showed plasticity. The data were calculated and plotted in the usual way and also according to dp/dt curves similar to those described by Coffman and Layng.¹¹⁶

Brückner and Ludewig¹³³ employed the same apparatus to determine the fusion be-

¹³² Bunte, K., Brückner, H., and Ludewig, W., *Glückauf*, **69**, 765-70, 950 (1933).

¹³³ Brückner, H., and Ludewig, W., *Brennstoff-Chem.*, **15**, 301-5 (1934).

havior of 2 noncoking (Fürst Leopold and Hohenzollern), of 3 coking (Heinitz, Gleiwitz, and Eschweiler) coals, and of the bright and dull constituents of these coals. Only the bright constituent of the coking coals showed both fusion and swelling. The dull portion of the Gleiwitz coal, because of its higher bitumen content, exhibited fusion without swelling and, therefore, was termed "pseudo" dull coal. Mixtures of dull and bright, older, coking coals gave reduced pressure resistances and shorter fusion ranges than the coals themselves. The data obtained were compared with crucible and volumetric degasification test results. Crucible tests gave higher contents of volatile matter for the corresponding dull coals; considerably higher than calculated averages for mixtures of coking coals; and somewhat lower than calculated averages for noncoking coals. The deviations were attributed to the mutual interaction of bitumens which affected their behavior on thermal decomposition. The volumetric gasification tests showed that the dull and bright coals yielded similar volumes of gas, despite the difference in content of volatile matter. Caking indexes for the mixtures lay between values for dull and bright coals, the bright coals having the highest.

Bunte, Brückner, and Sanjana¹³⁴ also used this method to determine the softening range of 10 Indian coals and of their petrographic constituents. The results were correlated with the results of proximate and ultimate analyses and ash-softening temperatures. Indian coals high in ash (12 to 13 percent) and in volatile matter (42 percent, dry, ash-free basis) produced good cokes because of their high content of β and γ constituents.

Brückner and Grevé¹³⁵ also used the method of Bunte, Brückner, and Ludewig¹³² to determine the plastic properties of a Saar gas coal (Heinitz) and a Ruhr coking coal (Zollverein), of certain of their petrographic constituents, and of blends of these constituents. The maximum pressure and the degree of swelling of the bright coal portions were higher than those for the coals themselves, whereas these values for the dull coal portions were lower. The fusain portion of the Heinitz coal showed small pressure. The Zollverein coal showed greater swelling than the Heinitz coal, but this order was reversed for the bright-coal portions. Swelling was reduced with increasing proportions of dull coal in the dull-bright coal blends. The swelling of a 90 : 10 bright : fusain blend of Heinitz coal was less than that of the 80 : 20 bright : dull coal blend. Pressures obtained by the gas-flow method for the blends did not correspond with those calculated from the mean values by the law of proportions.

Bunte and Imhof¹³⁶ also used this method to determine the plastic and gravimetric degasification properties of representative German coals: (1) a noncaking, sintering coal from Upper Silesia; (2) a nonexpanding, caking coal from the Saar district; (3) a coal from the Saar district intermediate in properties between these two; and (4-5) two expanding, caking coals, one from Upper Silesia, the other from the Wurm district. The 5 coals, in the order named, contained 38.6, 33.8, 34.2, 27.8, and 19.0 percent volatile matter (pure-coal basis), respectively.

Coal 1 showed only about 8 millimeters maximum water pressure at 420° C. Coal 2 gave a maximum pressure of about 1,000

¹³⁴ Bunte, K., Brückner, H., and Sanjana, J., *Brennstoff-Chem.*, **16**, 50-2 (1935); *Fuel*, **14**, 350-64 (1935).

¹³⁵ Brückner, H., and Grevé, H., *Brennstoff-Chem.*, **17**, 43-5 (1936).

¹³⁶ Bunte, K., and Imhof, H., *Gas- u. Wasserfach*, **82**, 805-12 (1939).

millimeters water pressure at 420° C with both a 10- and 5-gram sample. Coal 3 gave a maximum pressure of 450 millimeters water pressure at 440° C. Coal 4 showed a maximum pressure of 340 millimeters at 480° C, whereas coal 5 gave a maximum of 50 millimeters water pressure at 490° C.

Gas-flow tests were made on coal 4 after certain pretreatments which included studies of the effects of (a) standing in pyridine vapor for 10 days, (b) 15 percent addition of coke powder, (c) 1 percent addition of boric acid, (d) preheating in nitrogen for 4 hours at 390 and at 460° C, and (e) preheating in air for 4 hours at 150 and at 250° C. The maximum pressure of 340 millimeters water gage obtained in the Foxwell tests for the untreated coal was reduced by all treatments. Pyridine vapor treatment reduced the millimeters of pressure to 30, addition of coke powder to 75, addition of boric acid to 165, preheating in nitrogen at 390° C to 68 and at 460° C practically to zero, and preheating in air at 150° C to 14 and at 250° C to zero.

Kaatz and Richter²⁷ made a detailed examination of the gas-flow method. Studies on the effect of different grain sizes of coal showed that duplicate results could not be obtained with a grain size maximum of 0.2 millimeter. Maximum grain sizes of 0.49 and 1.02 millimeters gave corresponding "maximum resistance" values of 150 and 850 millimeters water-gage pressure. The 1.02-millimeter size was adopted as standard.

Classification of the "maximum resistance" values of 2 Westphalian, 5 Saxon, and 1 Silesian coals was made according to three groups: (1) less than 20 millimeters, (2) 20 to 100 millimeters, and (3) more than 100 millimeters. The maximum resistance developed by a blend could not

be estimated from those of the individual coals.

Lum and Curtis¹³⁷ studied the influence of various factors in the gas-flow method. The authors believed that, "with a given apparatus and a given coal, the variables which most influence the results obtained are presumably the following: rate of gas flow through the coal charge, packing of the crushed coal in the fusion tube, screen analysis of the coal used, and rate of heating as softening point is approached, and during the plastic stage." A review of certain earlier investigations, namely, those of Foxwell,¹⁰³ Layng and coworkers,^{112, 115, 116} Lloyd,¹¹⁸ Ball and Curtis,¹⁸ and Bunte and Löhr,¹³¹ revealed wide differences in the values selected for the five variables named above. After considerable preliminary study, Lum and Curtis chose a set of tentative standard values. By keeping all of them the same from test to test, except only the factor purposely changed for study, the extent to which each variable altered the results obtained was determined. The apparatus was essentially the same as that of Ball and Curtis,¹⁸ except that the gas pressure was measured in the gas space below the coal charge by a manometer connected near the bottom of the fusion tube. Temperature measurements taken in the center of the coal charge also eliminated the uncertainty of the temperature record observed by some earlier investigators.

The effects of these variables upon the course of the gas pressure-temperature curve for Lower Kittanning coal from Colver, Pa., were studied. It was found that rates of gas flow between 2.9 and 12 cubic centimeters per minute per square centimeter cross section of the coal tube did not affect the temperature of initial softening

¹³⁷ Lum, J. H., and Curtis, H. A., *Ind. Eng. Chem., Anal. Ed.*, **7**, 327-33 (1935).

(first increase in pressure) or the temperature of maximum resistance to gas flow. It was considered probable that very high rates would change these observed temperatures. The maximum gas pressure attained varied widely, even for the same rate of gas flow in successive experiments. Elimination of the fines below 50-mesh screen (30.6 percent) resulted in a slight increase in the initial softening temperature, a lower maximum pressure, and a less regular slope in the gas pressure temperature-curve for the higher temperatures. Rates of heating between 1 and 4° C per minute were found to give but little increase in temperatures of initial softening and of maximum pressures with increased rates.

Chandesris⁷⁷ used the Foxwell method at heating rates of 5° C per minute up to 325° C, and 2° C per minute from 325 to 500° C. Tests on Saar coals, before and after successive extractions with tetralin, pyridine, and quinoline, led to the following conclusions: (1) With removal of extractible material, real changes in the softening behavior were effected. However, tests on the residue after the triple extraction indicated that even with removal of carboids and certain humic materials the residue still possessed softening properties. (2) Gas permeability increased considerably more in dull than in bright coals toward the end of their softening, as indicated by the more rapid falling off of the last segment of the Foxwell curve. (3) The Foxwell curves of certain coals indicated individual points that appeared to be related to the beginning of melting of a bitumen whose melting point was always above 400° C and whose effect made itself evident by the marked fall of the curve at the end of softening. Such coals formed "spongy" cokes under these laboratory coking conditions.

TORSIONAL OR RESISTANCE OF MASS TO SHEAR TEST METHODS

Test methods measuring the resistance of the heated coal charge to shear caused by an applied known torque have received favorable attention since the pioneer work of Davis¹³⁸ in 1931. Two general adaptations of this principle have been made. In the Davis plastometer method the coal charge as a whole is rotated and stirred; the property measured is the resistance to shear of the partly fused coal adhering to the periphery of the retort. The resistance is created by the movement of the coal in the retort against rabble or stirring arms on an inside shaft, which is prevented from free rotation by a set of tension springs. With increase in the fluidity of the heated coal a decrease in the resistance, or torque, is noted. In the Gieseler plastometer method¹³⁹ the coal charge is static at first but is later stirred at a rate proportional to the fluidity developed in the coal. Rotation of the stirring shaft is caused by the application of a constant torque force on the shaft. With increase in fluidity of the heated coal, the rate of rotation of the stirring shaft increases.

Since 1931, extensive experience with this test method in the U. S. Bureau of Mines laboratories^{87, 88, 89, 90, 91} and elsewhere¹³⁹ has shown that the original design of the plastometer and the test principle of measurement were basically sound. Some of the constructional features of the original apparatus have been changed in minor respects to insure smoothness in operation of the apparatus.

Figure 5 shows a vertical section through

¹³⁸ Davis, J. D., *Ind. Eng. Chem., Anal. Ed.*, **3**, 43-5 (1931).

¹³⁹ Ver. Überwachung Kraftwirt. Ruhrzechen, *Jahresber. 1931-1932*, 35; *Glückauf*, **68**, 737 (1932); Gieseler, K., *Glückauf*, **70**, 178-83 (1934).

the plastometer in its present form. The technique used at present is to charge 18 grams of 0- to 20-mesh (Tyler sieve) coal into the retort, which is then fully assembled by screwing on the cap end connected to the thermocouple well. The retort is placed in the furnace, the thermocouple inserted in the well, and the retort rotated at a constant speed of 1.5 rpm. The elec-

formed is then quickly broken up, and resistance to rotation virtually ceases, thus indicating the end of the plastic temperature range. The resistance, or torque, necessary to prevent rotation of the inner shaft, caused by movement of the coal charge against the rabble arms, is measured by the position of an indicating dial with respect to a pointer index.

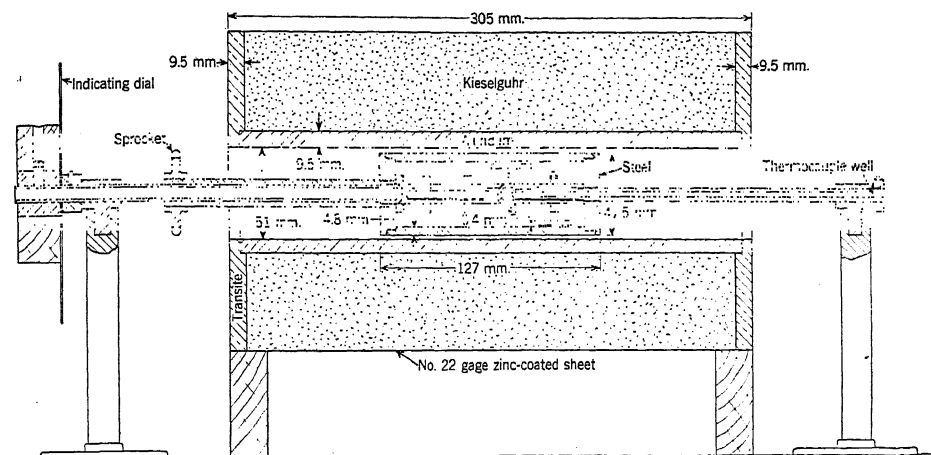


FIG. 5. Davis plastometer.^{90,138}

tric furnace is regulated to give an overall rate of heating of $4.8 \pm 0.2^\circ \text{C}$ per minute and a rate of $3.0 \pm 0.1^\circ \text{C}$ per minute from 300°C to the end of the test, around 500°C .

When the temperature of the plastic range of the coal is reached, the charge becomes viscous and resistance to rotation of the retort develops rapidly. With increasing temperature the resistance, after a slight increase, usually decreases, because the coal then attains its maximum fluidity. Some low-volatile bituminous coals do not show this decrease in resistance. As heating is continued, chemical and physical changes in the coal cause the charge to become more and more viscous and, finally, to solidify into semicoke. The coke

Corresponding temperatures and resistances are observed and recorded at 2- to 5-minute intervals throughout the entire plastic temperature range. Preliminary measurements of the temperature of the coal charge by a thermocouple inserted in the coal within the retort have established that the temperature here was 10°C lower than the corresponding temperature observed routinely by means of the thermocouple in its usual position in the thermocouple well. The observed temperatures were corrected to "true" temperatures of the coal charge by the addition of 10°C to each observed temperature reading.

The resistances, in pound-inches or kilogram-centimeters, are plotted as ordinates against the "true" temperatures as abscis-

sas. From these curves, it has been found possible to classify the plastic properties of bituminous coking coals and to show the relation of these properties to carbonization characteristics, both for coals of the different bituminous groups and for individual coals within these groups. Characteristic temperature points on the curve are: (1) the fusion temperature, at which resistance first develops; (2) the temperature or temperature range of maximum fluidity, at which the resistance again becomes low—the so-called “minimum resistance”; (3) the solidification temperature, at which the plastometer shows maximum resistance; and (4) the temperature defining the end of the plastic temperature range, at which the resistance becomes zero. Comparisons of these temperature points obtained on two different coals and the shape of their curves resulting from plotting temperatures in degrees Centigrade as abscissas against resistances in pound-inches as ordinates usually brings out information from which the coking properties of the two coals can be predicted with more or less certainty. For example, if the minimum resistance is high, or, as in some low-volatile coals, is not well-defined, the coal usually cannot be coked alone in a commercial oven without damage to the oven walls. When the temperature range of the maximum fluidity is long, namely, when the minimum resistance is low over a wide temperature range, the coal has well-defined fusion characteristics; in some instances, the coal is even too fluid to produce strong coke. A large maximum resistance indicates that such a coal should and usually does produce a strong coke. The plastometer test results also have been useful in indicating the composition of coals in respect to their petrographic composition and in the determination of the effect

of stepwise oxidation of coking coals on their coking properties.¹⁴⁰

Pieters and coworkers¹⁴¹ measured the torque resistance offered to a needle that moved laterally in an arc-shaped course through the heated coal charge. Six vitrain fractions selected from successive seams of the Limburg field showed that, with decrease in volatile-matter content (increase in rank) of the coals, the fluidity decreased, as shown by the increase in the minimum resistance values. The 4 coals with volatile-matter content ranging from 24.3 to 30.6 percent showed about the same order of fluidity, but the coal with 30.6 percent volatile matter did not maintain its fluidity over as long a temperature range as the other 3. The 2 low-volatile coals did not become nearly as fluid, and the fluidity did not last long. Such results agree with those by other workers.

The effect of the rate of heating was determined on the two low-volatile coals 5 and 6 containing 19.3 and 19.6 percent volatile matter, respectively, and on coal 3 containing 25.8 percent volatile matter. In the discussion of the data obtained, the authors stated, “We see that coal number 6, which when heated at a rate of 3° C per minute hardly softened at all, reaches a state of considerable fluidity when it is heated at the rate of 6 to 7° C per minute. Exactly the reverse takes place with a coal of lower rank.” Apparently, the authors intended the last sentence to apply to coal 3. In that sense, the conclusion was erroneous, because all the curves for the different rates of heating with each coal showed that the fluidity was increased in each coal

¹⁴⁰ Brewer, R. E., Holmes, C. R., and Davis, J. D., *Ind. Eng. Chem., Anal. Ed.*, **32**, 792–7, 930–4 (1940).

¹⁴¹ Pieters, H. A. J., Koopmans, H., and Hovers, J. W. T., *Fuel*, **13**, 82–6 (1934); see also Pieters, H. A. J., and Koopmans, H., *Het Gas*, **53**, 539–45 (1933); *Chem. Abs.*, **28**, 2500 (1934); and ref. 75.

with increased rate of heating. The false conclusions may have been due to a reverse order of tabulating the three rates of heating and also a reverse order of use of full, long dash, and short dash lines for the three curves of coal 3, as compared with the orders of tabulation and curve representations for coals 5 and 6.

Resistant plant remains as they occur in durains caused little change in the temperature range of plasticity but lowered the attained fluidity. The effect of oxidation was to shorten the plastic temperature range and lower the fluidity of the coal. Coal 3, when heated at 3° C per minute, gave a plastic temperature range of 413 to 522° C and 2.5 grams minimum resistance. The width of the plastic range was shortened and the maximum resistance was increased by preheating the coal in an oxygen atmosphere. Heating for three quarters of an hour at 200° C resulted in a plastic range of 420 to 489° C and a maximum resistance of 9 grams, and for the same time at 250° C a plastic range of 441 to 489° C and a maximum resistance of 15 grams.

The influence of increased pressure used in briquetting the coal charge was to give a wider temperature range of plasticity. Beyond a pressure of 2,500 kilograms per square centimeter the effect was not appreciable. This latter pressure was used as standard in all the tests whose results have been cited above.

In their later paper,⁷⁵ Pieters and co-workers reported results obtained at a heating rate of 2° C per minute on 13 vitrains, ranging in volatile-matter content from 16.8 to 34.8 percent (dry, ash-free basis). The lowest temperature at which fluidity could be measured was higher by this torsion method than the beginning of fusion as determined at the same rate of heating by their dilatometer method. The coal

also was still fluid at the temperature at which expansion was completed in the dilatometer test, thus showing that the so-called solidification temperature by the dilatometer method really represented a state of equilibrium between the internal pressure developed in the coal charge and the external pressure of the dilatometer piston on the charge. Temperatures at which the 13 coals attained the same fluidity in the torsion method were joined in a diagram in which these temperatures were plotted against the fusion points of the coals. Areas defined by fluidities of 0, 2, 5, 10, and 25 scale readings were called "lakes of fluidity" and showed that only a limited number of coals were fluid enough, for a given rate of heating, to be considered coking coals.

Gieseler¹¹⁰ used a coal charge that was static at the start of the test and that was stirred later at a rate dependent upon the fluidity of the heated coal. The resistance to stirring, or torque, was measured in terms of the rate of rotation of a stirring shaft under the application of a load of 75 or 100 grams on a loading pan. Heating was carried out at a rate of 3° C per minute. The rate of rotation increased with increased fluidity of the coal to a maximum at "maximum fluidity" (highest value of plasticity), and then decreased to zero at the "point of resolidification" of the coal. The temperature difference corresponding to this period of rotation was designated as the "softening zone." Readings of temperatures in degrees Centigrade and pointer movements in angular degrees on the circular scale were made each minute.

Six Ruhr, four Lower Silesian, and four Upper Silesian coals—one a blend—whose softening properties had been determined by the Schimmel penetrometer method in an earlier investigation²⁴ were tested by

the torsion method. Gieseler stated that the samples had been stored for more than a year in well-closed, glass-stoppered vessels, and that the Silesian coals especially had lost their caking capacity. Strangely, however, the softening zones reported by the two methods used in the two investigations showed excellent agreement.

In the Ruhr coals (volatile-matter content, 17.3 to 26.0 percent, pure-coal basis) the maximum value of plasticity (maximum fluidity), expressed in angular degrees, increased regularly with increase in volatile matter, or decrease in rank, of these coals. The Lower Silesian coals (volatile matter, 24.7 to 34.0 percent, pure-coal basis) did not show much regularity. The values of maximum plasticity were between 14 and 39, but not in the strict order of the volatile content. The Upper Silesian coals (volatile matter, 29.6 to 36.2 percent, pure-coal basis) showed a decrease in their maximum plasticity values with increasing content of volatile matter. Excluding, for the moment, the Lower Silesian coals, the maximum values of plasticity increased regularly with decreasing rank of the coals through the Ruhr coals up to the Upper Silesian gas coal containing 29.6 percent volatile matter (pure-coal basis) and then decreased regularly. This general trend has been observed also by later workers.^{142, 65, 91} The relationship is not strictly a linear one. Oxidation and petrographic composition modify the relation to a great extent and may account for the irregularities.

Gieseler plotted the plasticity number expressed in angular degrees as ordinates against temperature in degrees Centigrade as abscissas. Readings in angular degrees below 1 were plotted on a tenfold scale to those above 1, so as to show more clearly the beginning of softening and the ap-

proach of solidification of the coal. He also defined a temperature "zone of greatest plasticity," apparently the range corresponding to readings of 1 or more angular degrees for coals of low fluidity and to 10 or more for coals of higher fluidity, as nearly as the tabulated data can be determined from his plotted curves.

Gieseler studied the effect of heating rates of 1, 3, and 6° C per minute upon the plasticity curves of a representative coal from each district. With increasing rate of heating, the temperature of softening was little affected; but the temperature zone of softening, the resolidification temperature, and especially the degree of plasticity were increased. In discussing these results Gieseler stated that

On account of the slower heating the generated gases and vapors have sufficient time to escape from the coal cylinder, whereas with more rapid heating the vapors and tar fog remain in contact with the coal for a longer time and produce a plastic paste. This is in harmony with the fact that with greater rates of coking the quality of the coke becomes better and the coke on the heated walls of the oven chamber is always more dense and appears better melted than in the middle of the chamber where the smallest rate of heating prevails.

The present writer believes that the composition of the volatile products varies with different rates of heating. With more rapid heating the proportion of plastic material is increased. Furthermore, coals of high rank remain plastic to a higher temperature and leave less volatile matter to be evolved after plasticity has ceased. Certain coals have shown themselves to be remarkably sensitive, with respect to their ability to yield a good coke, to changes in the average rate of heating, so that to produce the best coke an appropriate rate of heating for each individual coal must be used.

¹⁴² Jung, G., *Glückauf*, 71, 1141-8 (1935).

Bleibtreu and Jung¹⁴³ determined the plasticity of 3 coking coals by the Gieseler method, using the added load of 75 grams. Plasticity "numbers" (presumably angular degrees) of 114, 103, and 122 were obtained for Bahnschacht, Tiefbau, and a blended coal "Cokery," respectively. Tiefbau coal also was tested at heating rates of 2, 3, 3.5, and 4° C per minute. With more rapid heating the plasticity was found to increase and the resolidification point was shifted to a higher temperature.

Jung¹⁴² incorporated certain changes in the Gieseler test method that improved the operation, especially with very strongly softening coals. He attempted to calibrate his plastometer by means of standard pitches whose viscosities had been determined previously by the test method of Reerink and Goecke,¹⁴⁴ but unfortunately, the two equations given by him for the test pitches contained errors. The calibration tests, on account of the impossibility of measuring viscosities larger than 10 gram-seconds per square centimeter, signified no exact values, but they did indicate the order of magnitude of the viscosity of the coal melt and with it the plasticity of the coal.

Jung also investigated the effect of oxidation on the softening temperature zone and the magnitude of plasticity in this zone for 6 Lower Silesian coals. The coals included: (1) Bahnschacht, Seam 17; (2) Bahnschacht, Seam 16; (3) Tiefbau (Hans-Heinrich- and Marie-Schacht Seams), washed fine coal; (4) Bahnschacht, washed fine coal; (5) Bahnschacht, Seam 5; and (6) an 82 to 18 percent blend of coals 4 and 3, respectively. Samples of 90 grams and known grain size were placed in shal-

low dishes of 135 square centimeters top surface, and inserted 4 at a time in a gas-tight drying cabinet of 10-liter capacity. The temperature of the cabinet was regulated automatically at 100, 60, or 20° C, as desired, and air passed through at a rate of 300 cubic centimeters per minute. At fixed time intervals, 12-gram portions of the samples were removed and tested for their plastic properties in the modified Gieseler plastometer. Determinations of the oxygen consumed by the coal at various temperatures and times in the series of tests were made and reported. For example, at the test temperature of 100° C about 600 cubic centimeters of the total oxygen from the 18,000 cubic centimeters of air introduced per hour was used by the coal.

Samples 1 to 5 were caking coals, containing 24.6 to 30.2 percent volatile matter (pure-coal basis). The coals, in 0- to 0.5-millimeter size, were aged at 60° C for 36, 110, 210, 310, 500, and 700 hours. The softening temperatures (beginning of softening) and the solidification temperatures (end of plastic zone) of coals 1 and 2 were little affected by increased time of aging. The softening temperatures of coals 3, 4, and 5 increased, and their solidification temperatures tended to decrease under the same test conditions. Accordingly, the width of the plastic zone either remained the same or was smaller. These results, in part, were in contrast to those determined from Foxwell curves, which depend on the peculiarities of the method.

The maximum plasticity numbers (angular degrees per minute) by the plastometer method at first dropped rapidly and then more slowly with increased time of aging of the coal samples; corresponding temperatures fell but slightly. With reduction of the maximum plasticity numbers to about 100, the Meurice-Campredon

¹⁴³ Bleibtreu, H., and Jung, G., *Glückauf*, **70**, 733-40 (1934).

¹⁴⁴ Reerink, W., and Goecke, E., *Glückauf*, **71**, 77-85, 105-14 (1935).

caking numbers^{35a, e, p} decreased only slightly; thereafter, the decrease was more pronounced.

The rate of change in properties of the 5 coals became quite slow after they had been oxidized for 700 hours at 60° C. Extrapolation of the experimental curves (plasticity numbers as ordinates versus aging times in hours as abscissas) showed that coals 1 to 5, after oxidation at 60° C for 820, 800, 700, 1,000, and 800 hours, respectively, reached the same plasticity values that were obtained after oxidation at 100° C for 50 hours.

Coal 6 (over 2 millimeters in size) was a coking blend used in a commercial coking plant. A screened (2 to 4 millimeter) sample of this blend was carefully pulverized and sieved to obtain 0 to 0.5, 0.5 to 1, 1 to 2, and 2 to 4 millimeter fractions of 0.3, 0.75, 1.5, and 3 millimeter average grain size, respectively. The three smaller size fractions were aged in the described apparatus at 100° C in steps of 8, 16, 24, 48, 96, and 215 hours, and the 1 to 2 millimeter size also was aged for 430 hours. The largest size (2 to 4 millimeters) fraction was aged similarly for 48, 96, 215, and 430 hours. With increased time of aging all four fractions showed increases in their softening and decreases in their solidification temperatures; the width of their softening zones, therefore, became shorter. At the same time the maximum plasticity numbers fell off, and their corresponding temperatures, as well as the caking numbers, also decreased. However, the velocity of change in plasticity increased with decrease in grain size of the samples. The plotted results, using maximum plasticity numbers as ordinates and aging times in hours as abscissas, gave a series of hyperbolic curves whose distances from the axes increased with increasing grain size of the coals. The caking numbers plotted as or-

dinates against the aging times as abscissas showed a more linear decrease of caking numbers with aging time. From these curves, like plasticity numbers and like caking numbers were compared with their corresponding aging times. The logarithms of these times were plotted as ordinates against the logarithms of the four grain sizes as abscissas. Since the aging times are proportional to the grain diameters, the lines of equal plasticity or equal caking power follow a course of about 45° to both axes in the diagram. The plotted results showed that this was closely approached, being slightly under 45° to the abscissas' axis, and becoming less with longer aging times, especially for the larger size grains. This change was attributed to fissure formation developing in the larger grains and thereby an increase in surface. Accordingly, it could be concluded that the velocity of aging was proportional to the surface, or in inverse ratio to the determined grain size of the coal.

The coal blend in a grain size of 0 to 0.5 millimeter was oxidized at 100° C for 8, 16, 24, and 48 hours, at 60° C for 72, 120, 216, 384, and 768 hours, and at 20° C for 1,296 and 1,920 hours. For each temperature of treatment, the temperature of the beginning of softening was increased, the temperature of solidification was little affected, and the maximum plasticity number, the corresponding temperature, and the caking number were decreased with increasing time of oxidation.

The logarithms of the plasticity numbers in each case were plotted as ordinates against the logarithms of the times of oxidation as abscissas. The three resulting curves, sloping downward toward the right, were approximately straight lines parallel to each other. The horizontal distances between equal plasticity numbers showed values of log 15 between the 100° and

60° C curves and log 23.8 between the 60° and 20° C curves, respectively. The quotients of the oxidation times at 20° divided by those at 60° C, and those at 60° divided by those at 100° C, all corresponding to the same plasticity numbers, were thus between 15 and 23.8. In other words, raising the temperature 40° C in the temperature range from 20 to 100° C caused a 15- to 23.8-fold increase in the aging velocity. Since the temperature coefficient between 20 and 60° C was the same as that between 60 and 100° C, the temperature coefficient for each 10° C was then the fourth root of the quotient numbers, giving experimental values between 1.96 and 2.20. A temperature increase of about 10° C, therefore, corresponded to doubling the velocity of aging. This rule was checked from data obtained on coals 1 to 5 after oxidation at 60° C for times necessary to give the same plasticity numbers as obtained after oxidation at 100° C for 50 hours. The fourth roots of the quotients obtained from the data on the 5 coals were between 1.93 and 2.12, or an average of 2.02, which checked well with values obtained on the blended coal.

Schroth¹⁴⁵ found that the current taken by a motor for driving the Gieseler stirring device could, with suitable prudence, be considered a measure of the magnitude of the viscosity of the coal. The method was claimed to be generally practicable. Comparisons of the characteristic temperatures of the beginning of fusion and of resolidification found by this method with the corresponding temperatures on Foxwell curves showed good agreement. The plastic temperature range of a correctly surveyed Foxwell curve could be determined, and this curve, within certain limits, also permitted some conclusions on the actual plastic state of the coal. Conclusions on the course of

the viscosity and on the temperature points of the greatest fluidity could be made from the results of the Gieseler method.

The U. S. Bureau of Mines modification of the Gieseler plastometer has been described by Brewer and Triff.⁹¹ Figure 6 shows a sectional drawing of the apparatus. The steel retort has an inside depth of 16 millimeters and an inside diameter of 21 millimeters; in contrast with the retort of Gieseler¹¹⁰ and the high-form retort of Jung¹⁴² it has no sieve plate above the coal charge at the top of the retort. The frequent binding between the stirrer shaft and the sieve plate, caused by the accumulation of partly carbonized heavy tars, is thereby eliminated. Extended experience without the use of a sieve plate has shown that in only a few very strongly swelling coals does the heated coal mass creep up above the top edge of the retort to an extent that the rate of rotation of the stirring shaft is affected. In testing very strongly contracting coals, the softened charge may be carried bodily around the rotating stirring shaft. To avoid the false indication of a highly fluid mass in such coals, a steel pin 1.6 millimeters in diameter is inserted through a hole in the wall of the retort at a point 5 millimeters from the top edge and to a distance of 5 millimeters radially toward the center of the retort from the inside wall.

The charged retort is assembled, as shown in Fig. 6, and lowered into the metal bath, preheated to 340° C, after which heating is maintained at 3° C per minute. A 20-gram weight on the 18.7-gram loading pan is enough to cause uniform rotation of the stirring shaft in the empty retort, no rotation in the coal charge until initial softening of the coal is reached, and a smooth movement during the passage of the coal through the pre-plastic and plastic temperature ranges. At

¹⁴⁵ Schroth, W., *Angew. Chem.*, **49**, 567 (1936).

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the initial softening temperatures of the coal the loaded pan starts to fall and continues falling to the end of the test.

This initial softening temperature is taken at the first appreciable movement of the pointer, that is, 0.1 dial division on the 100-scale-division dial. From this point on, corresponding readings of time, temperature, and pointer movement are made at 1-minute intervals. From observed

times, temperatures, and dial readings the corresponding number of pointer revolutions is calculated in dial divisions per minute. Dial divisions per minute correspond to fluidity of the coal at the various temperatures; they increase to a maximum and then decrease again to zero. Curves are constructed showing dial divisions per minute plotted as ordinates against temperatures in degrees Centigrade as abscis-

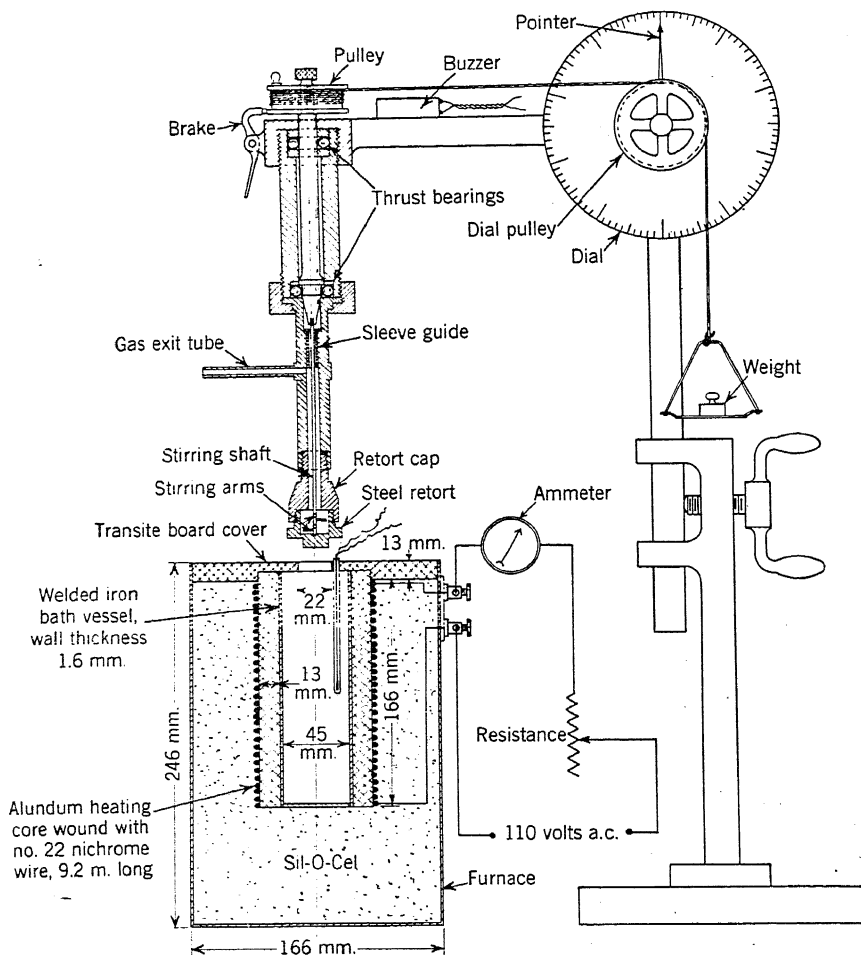


FIG. 6. Modified Gieseler apparatus.²¹

sas. The fusion temperature is taken as the temperature corresponding to 5 dial divisions per minute on the ascending portion of the curve; the temperature of maximum fluidity, as the temperature at which the stirring shaft shows the most rapid rate of movement; the solidification temperature, as the temperature corresponding to 5 dial divisions per minute on the descending portion of the curve; and the end of the plastic range, as the temperature at which the pointer again shows no movement. For coals of low fluidity the fusion and solidification temperatures are taken at 0.5 dial division per minute. The preplastic temperature range is defined as that between the initial softening temperature (0.1 dial division) and the fusion temperature. The plastic temperature range includes the temperature range between the fusion temperature and the end of the plastic range.

Kushnarevich¹⁴⁶ determined the resistance offered to rotation of a corrugated iron disk immersed in coal powder. The resistance rose at about 450° C, fell sharply at 475 to 525° C, rose to a second maximum at 525 to 550° C, and then fell rapidly to a constant value coinciding with solidification of the mass. In a second paper¹⁴⁷ Kushnarevich stated that a coal sample was placed in a specially constructed vessel, and a rotating disk was pressed against the top of the charge with a definite pressure while the coal was being heated from the bottom. The coal charge was heated to 280° C in about 20 minutes; the disk then began to rotate, and the temperature was raised to about 580 to 610° C at any desired rate. Curves showing the force of rotation plotted against

temperature were constructed and explained.

Macura¹⁴⁸ attempted to express the concept of "coal plasticity" in terms of the reciprocal value of the viscosities of the fluid, gaseous, and solid phases in combination with the phenomena of elasticity of all three phases of the coal developed during heating. Disregarding the unknown effects of elasticity, as a first approximation, the softening behavior of a coal could be well characterized as "froth fluidity," made up of the fluid phase (softening bitumens), the gaseous phase (distillation gases and vapors), and the solid phase (nonplastic residual coal). It might seem inaccurate in such a heterogeneous system to consider "froth fluidity" as representative of such crude approximate conceptions. However, for the time being, the measure of the "total softening" or, more properly, the "total fluid power" of coal, which admittedly still lacked an exact definition, could be best expressed by the term "fluidity" or "froth fluidity." The "total softening" or "total fluid power" of a coal was represented by Macura as the area under the differential curve showing plasticity values plotted as ordinates against temperatures or times as abscissas.

After using the Gieseler plastometer¹¹⁰ with limited success, and after a great deal of further experimentation with other designs of his own, Macura finally developed a plastometer, which, because of its many parts and complicated construction, was described in minute detail. For a complete description, the interested reader should refer to the original publication.¹⁴⁸

Special features of the Macura plastometer included a cylindrical, nickel-chromium steel retort whose hemispherical bottom and inside wall were cut by triangular

¹⁴⁶ Kushnarevich, N. R., *Coke and Chem. (U.S.S.R.)*, 8, No. 10, 24-6 (1938).

¹⁴⁷ Kushnarevich, N. R., *Zavodskaya Lab.*, 9, 1119-22 (1940); *Chem. Abs.*, 35, 1603 (1941).

¹⁴⁸ Macura, H., *Oel, Kohle, Erdoel, Teer*, 14, 1097-1107 (1938), 15, 1-12 (1939).

grooves. Centered in the retort was a stirrer of the same material consisting of a vertical hollow tube with a ball on its bottom end. The surface of the ball also was cut by triangular grooves. Temperatures at the center of the ball were measured by a calibrated thermometer, inserted down through the hollow tube. The stirrer extended upward to a framework, which supported a vertically mounted mirror and a horizontally mounted cord pulley and which could be rotated about the axis of the pulley by the application of a torque force or load. The angular displacement was measured by noting the angular movement of a light beam reflected from the mirror on a graduated, arc scale (D'Arsonval principle). One angular degree of rotation corresponded to 87.267 millimeters on the scale.

The plastometer was standardized with an asphalt whose viscosities at 20, 15, and 14° C had been established in a modified falling ball Höppler viscosimeter as 0.4333×10^6 , 1.4428×10^6 , and 1.98×10^6 poises, respectively. Data from 66 tests were expressed as "products," obtained by multiplying the turning time per angular degree, in seconds, by the applied load, in grams, and by the length (3.5 centimeters) of the lever arm. Tests with loads of 8 and 16 grams at 20° C gave the same "product," 431.2, but in the two series of tests at 15 and 14° C the "products" decreased with increasing load, showing that the viscosity of the asphalt at these two lower temperatures depended on thrust pressure. Curves with these "products" plotted as ordinates against load as abscissas showed that the curves up to a load of 8 grams were bent strongly downward, because of friction in the apparatus. Beyond this load the curves were linear and were inclined downward with increasing load; the slope of the curve for tests at

15° was less than that of the curve for tests at 14° C. "Products" obtained at the three temperatures with the 8-gram load when multiplied by a constant 1.005 gave approximately the values in poises, cited above for the viscosities of the asphalt, as determined at these same temperatures in the modified Höppler viscosimeter.

The coal sample, previously crushed to pass more than 98 percent through 0.5 millimeter and then dried, was charged and compressed under a standard pressure to a fixed height in the retort. The charged assembled apparatus was immersed in a preheated salt bath, and the rate of heating was then controlled, as desired, for the particular test.

Lower Silesian coal *a* was tested with a 16-gram load at average rates of heating of 1.53, 2.98, 6.47, 9.70, 12.93, and 14.60° C, and with an 8-gram load at average rates of heating of 1.46, 3.20, 6.45, 9.60, and 14.60° C. *Mean* or summation curves for data from two or more tests at each of these loads and rates of heating were constructed. The abscissas represented temperatures of the coal sample during the test, in degrees Centigrade, and the ordinates showed the corresponding progression of light-beam movement over the arc scale, in total millimeters. The ordinates also were expressed in equivalent rhe-seconds and rhes. *Differential* curves were derived from the corresponding *mean* curves. The abscissas again represented temperatures in degrees Centigrade, and the ordinates were expressed in both rhes and poises. Also, *mean* curves were constructed and *differential* curves were derived for data from tests of Upper Silesian coal *b* with a 16-gram load and average rates of heating of 1.55, 3.25, 6.46, 9.81, 12.96, and 14.70° C, and with an 8-gram load and average rates of heating of 3.11, 6.46, 9.79, and 14.84° C, and for data

from tests of Lower Silesian coal *c* with a 16-gram load at average rates of heating of 3.05, 6.65, 10.04, and 13.26° C per minute.

The data were expressed most characteristically by "viscosity in poises" and "maximum fluidity in rhes" at the maximum of the differential curve, and as "mean fluidity in rhes" and "total fluid power in rhe-seconds" for the entire softening process.

Comparison of the curves for the 3 Silesian coals obtained by plotting the total fluid power in rhe-seconds as ordinates against the rates of heating in degrees Centigrade per minute as abscissas showed that the total fluid power became greater with increased rate of heating. The slope of the curves for coal *a* indicated that the total fluid power increased more strongly for rates of heating of temperature ranges 0 to 3° C and 10 to 15° C per minute than for rates of 3 to 10° C per minute. Also, particularly, in the last range, the curve for the 8-gram load represented a higher total fluid power than the curve for the 16-gram load. At rates of heating higher than about 1.5° C per minute coal *b* showed almost a linear increase in total fluid power with increasing rate of heating; the curve for the 8-gram load showed only a slightly greater total fluid power than that of the 16-gram load over the entire range of rates of heating. The curve for coal *c* for the 16-gram load fell between the two curves for coal *a* and the two curves for coal *b*. From the course of the five curves one must conclude that the total fluid power observed with increasing rates of heating depended on the rate of heating and, further, that each curve gave information on the softening behavior of the coal under different thrust pressures and rates of heating; that is, the curve has a separate characteristic

form and position for each measured system for each coal. Probably, the relative amounts and composition of the petrographic components also have an important effect upon the form and position of the curves.

Aside from the quantitative dependence of the softening process on the rate of heating, a qualitative dependence was shown also. The data obtained for individual coals in series of tests made with a given load and various rates of heating when plotted, using rhes and poises as ordinates against degrees Centigrade as abscissas, gave a family of differential curves. The curves representing the lower rates of heating fell under those for higher rates of heating. Furthermore, the curves for the same coal at like rates of heating but different thrust pressures showed that those for the higher thrust pressure (16 grams) had lower softening points than those for the lower thrust pressure (8 grams). In each series of tests the temperature at which maximum fluidity developed increased with increased rate of heating. The geometric loci of the maximum points on the curves for coals *a* and *b* were parabolas; those for coal *c* formed a straight line. The points of resolidification of the coals also were displaced to higher temperatures with increased rates of heating, that for coal *c* being especially marked—from 445 to 470° C for the increase in rate of heating from 3.05 to 13.26° C per minute. In brief, then, the characteristic effects of increased rate of heating were to broaden the temperature interval representing the plastic range and to increase the degree of fluidity of the coal.

Macura pointed out that the practical importance of the type of measurements he described lay in the fact that, by regulating the thrust pressure and rate of heating, the softening process of the coal could

be determined under appropriate conditions. The data, when studied in connection with the results of degasification tests on the coal for temperature intervals before, during, and after the plastic temperature range as shown by plastometer tests, should have direct application to coke-plant practice. With the introduction of the concept "total fluid power," expressed as a measurable unit in the cgs system, the entire softening process of the coal can be established quantitatively by a *single number*, which with uniform composition and grain size of the coal depends only on the rate of heating and thrust pressure.

Macura discussed the limitations of his test method. The method is not applicable for testing coals with a caking index¹⁴⁹ below 8, for these coals, especially at lower rates of heating, do not fuse completely. The use of a sample having a grain size larger than 2 millimeters is not possible on account of nonuniform heating through of the coal particles in the 3-millimeter space between the ball and the rounded bottom of the retort. For feebly swelling coals, the shaft must be loaded with 400 to 500 grams to avoid raising it out of the retort and also to maintain a constant volume of charge. Tests with strongly swelling coals are not reproducible. Macura stated that he attempted to suppress the swelling of such coals by the addition of plasticity leaning materials and before measuring the softening process. The compression of the coal charge under a pressure of 47.25 kilograms per square centimeter was considered a disadvantage but was found to be necessary to obtain concordant results.

In a second paper¹⁵⁰ Macura compared the differential curves representing the

plastic properties of the coals *a*, *b*, and *c* previously studied¹⁴⁸ and of Upper Silesian coal *d* with the results of gravimetric differential distillation analyses made on the 4 coals. These analyses gave the gravimetric yields of semicoke and volatile matter, together with the subdivision of the volatile matter into tar, water of decomposition, and gas (by difference), at rates of heating of 3, 6, 9, and 13° C per minute over the temperature range from 300 to 550° C. Weighings were made at 30-second intervals for the lower rates of heating, and at 15-second intervals for the higher rates. The elaborate test arrangement will not be described here.

The data for total volatile matter, tar, water of decomposition, and gas obtained by the gravimetric differential distillation tests were expressed in percentages by weight of dry coal for each 5° C rise in temperature. These percentages for each rate of heating (3, 6, 9, and 13° C per minute) were plotted as ordinates against temperatures in degrees Centigrade as abscissas for the temperature range from 300 to 550° C. On the same charts were reproduced the differential curves representing the plastic properties of the same 4 coals for the same rates of heating. The ordinates represented the fluidities of the coals expressed in rhes and poises; the abscissas, the corresponding temperatures in degrees Centigrade. The weight percentages both of water of decomposition and of gas did not vary enough under the test conditions to warrant any conclusions on their relationship to the plastic properties of the coal.

For coal *a* the maximum values of total degasification (total volatile matter) and of tar were displaced with increased rates of heating in the direction of higher temperatures, reaching the neighborhood of the temperatures of resolidification of the

¹⁴⁹ Kattwinkel, R., *Glückauf*, **62**, 972-3 (1926).

¹⁵⁰ Macura, H., *Oel, Kohle, Erdoel, Teer*, **15**, 45-54 (1939).

test samples at the higher rates. Coal *b*, in spite of its essentially lower fluidity, behaved in a similar manner. Coal *c* with increasing rates of heating showed that the maximum values of total degasification and of tar were obtained at temperatures above the resolidification temperatures of the test samples. Coal *d* showed a converse effect with increased rate of heating. Displacements of the total degasification and tar curves were to lower temperature ranges. From the results obtained at the four different rates of heating for each of the 4 coals, one may select conditions under which the maxima of the curves for plasticity, total degasification, and tar are in proper relationship to each other to produce the best grade of coke.

Macura gave no data on the geological sources, petrographic composition, or ultimate analyses of the 4 coals. The ash contents of coals *a*, *b*, *c*, and *d* were given as 4.8, 13.1, 25.8, and 9.6 percent (as tested), respectively. Corresponding dry volatile-matter contents by the Bochum crucible test were 32.6, 30.3, 22.3, and 33.1 percent.

Hoehne⁶⁵ made more than 3,000 tests with an apparatus and test procedure essentially like those of Jung.¹⁴² The usual plasticity curve, angular degrees per minute plotted as ordinates against temperature in degrees Centigrade as abscissas, defined the plastic zone as the temperature interval between the beginning of softening and the resolidification of the coal mass. In common with the experience of other workers, for example, Gieseler¹³⁹ and Brewer and Triff,⁹¹ Hoehne found that at the beginning of softening of the coal, probably on account of the liberation of gases from the coal charge, false readings (movements of stirrer) sometimes were shown in the torsion type of test method. He, therefore, defined arbitrarily

the "limits of an active plasticity zone." For coals containing an average of 27 percent of volatile matter, as well as those with a higher content, about 34 percent (pure-coal basis), his preliminary tests established that a dial reading of 20 angular degrees must be obtained before such coals formed a well-caked semicoke at the standard rate of heating of 3° C per minute; with coals showing limited plasticity (maximum dial reading up to about 40 angular degrees) a reading of 9 angular degrees was considered the lowest at which the coal would normally form a well-caked semicoke at this rate of heating. Therefore, the "effective" or "active plasticity zone" was defined by Hoehne as the portion of the usual plasticity curve above ordinate values of 20 and 9 angular degrees, respectively, for these two classes of coals.

Hoehne reported data on the plastic properties and volatile contents of 51 coals and 4 blends from the Ruhr district and on "standard drum" tests of cokes (presumably from both box tests and a small carbonizing chamber) made from these coals and blends. He stated that the drum strength tests on cokes from box tests were always 2 to 3 percent lower than on cokes from the chamber and, hence, were directly comparable.

The coals were classified into groups according to percentage of volatile matter (pure-coal basis), as follows: *lean* coals (*m*) 10–19; *lean fat* coals (*mfe*) 19–24; *fat* coals (*fe*) 24–30; *gas* coals (*g*) 30–35; and *gas flame* coals (*fl*) 35–40. They included: 1 Westphalian and 3 Lower Silesian lean coals; 5 Westphalian and 5 Lower Silesian lean fat coals; 1 Upper Silesian, 6 Westphalian, and 9 Lower Silesian fat coals; 3 Westphalian and 10 Lower Silesian gas coals; and 2 Westphalian, 3 Upper Silesian, 1 Saxon, and 2 Saar gas flame coals. The four blends of fat and gas coals con-

tained between 27 and 28 percent volatile matter (pure-coal basis), which placed them in the fat-coal group. It was not stated which individual Lower Silesian and Westphalian coals were used in making these blends.

Hoehne represented his test data in seven composite diagrams, with different arrangements of data to bring out certain properties of the coals and coal blends. These diagrams have been assembled and the data rearranged in a single, similarly constructed diagram, Table II, to which has been added a column tabulating the width of the active plastic range temperatures in degrees Centigrade for the 51 coals and 4 blends.

Table II shows the coals and blends arranged in order of increasing maximum fluidity up to the maximum value of about 35,000 angular degrees and then in order of decreasing maximum fluidity. The coals are designated by the initial or first two letters of the German name of the locality where they were mined, by the group symbol, and by a number if more than one coal from a given locality and group was tested; for example, niederschlesische Magerkohle 2, *Nm* 2 (Lower Silesian lean coal 2), ober-schlesische Fettkohle, *Ofe* (Upper Silesian fat coal), and sächsische Gasflammkohle, *Safl* (Saxon gas flame coal). The four blends are designated by the symbols *Nk* 1, *Nk* 2, *Nk* 3, and *Nk* 4. The width of the "active plastic zone" or temperature range in degrees Centigrade is represented graphically for each coal or blend by the sum of the lengths of its two heavy or two dashed lines plus the space between them. This space covering a temperature interval of 3° C corresponds to the temperature at which the coal or blend showed its maximum fluidity. In general, it will be observed that, according to the arrangement shown of the coals and blends in Table II, the width of the active plastic range, in

degrees Centigrade, and the coke strength from a standard drum test, in percentage, change in a corresponding manner, but that the rank decreases (pure volatile matter increases) throughout. By this arrangement *lean fat* coals and *fat* coals as well as their 4 blends are separated rather sharply from the *gas* and *gas flame* coals. The order of regular increases in volatile matter is not maintained within these classifications, but the general tendency from the top to the bottom of the diagram shows an increase in the volatile-matter content. In general, it may be noted also that the temperature limits defining the "active plastic range" are displaced to higher temperatures up to the coals of maximum fluidity, and then are displaced to lower temperatures as maximum fluidity decreases. No one arrangement of data has given entirely consistent linear relationships between any two sets of data.

It may be pointed out that the Lower Silesian *lean fat* coals, *Nmfe*, showed less fluidity as a group than the corresponding Westphalian *lean fat* coals, *Wmfe*; the same trend was noted for the *fat* coals from these districts. With few exceptions, the gas flame coals were less fluid than the gas coals. These general trends are in harmony with the relative ranks of the coals.

EXTRUSION METHODS

This class of test employs an apparatus having an orifice through which the softened heated coal is forced under applied pressure. The data obtained have been applied qualitatively in interpreting some of the phenomena observed while the coal is fluid and in explaining some of the weak features of other methods. However, lack of test conditions similar to those prevailing during actual coking of a coal charge in commercial coke ovens and the difficulty of obtaining quantitative duplicate data in

TABLE II

COMPARISON OF "ACTIVE PLASTIC ZONE," MAXIMUM FLUIDITY, AND VOLATILE-MATTER CONTENT OF REPRESENTATIVE GERMAN COALS AND BLENDS WITH STRENGTH OF THEIR RESULTANT COKE,^{1, 65}

Coal No.	Temperatures, °C										Width of Active Plastic Range, °C	Maximum Fluidity, Angular Degrees	Standard Drum Coke Strength, Percent	Pure Coal Volatile Matter, Percent
	401	410	419	428	437	446	455	464	473	482	491			
Wm											—	—	—	10.6
Nm 1											—	—	—	16.3
Nm 2							---				7	8	14.5	18.0
Nm 3							---				12	8	57.5	18.5
Nmfe 1							---				15	10	75.0	19.1
Nmfe 2							---				22	12	69.0	20.6
Nmfe 4							---				24	13	68.0	22.8
Nmfe 5							---				27	16	71.3	22.9
Nfe 3							---				33	21	68.5	25.5
Nmfe 3							---				22	22	68.0	22.4
Nfe 1							---				36	41	68.0	24.1
Nk 3							---				39	170	65.9	27.8
Wmfe 3							---				45	197	75.0	22.4
Nk 4							---				42	240	65.0	27.5
Nfe 2							---				45	280	82.0	24.5
Nk 2							---				45	310	67.1	27.2
Nfe 6							---				45	310	67.1	27.2
Nfe 5							---				42	390	76.0	26.3
Nk 1							---				48	400	69.6	27.6
Wmfe 5							---				51	464	73.0	23.6
Nfe 8							---				45	565	75.2	25.5
Nfe 4							---				42	570	71.1	25.8
Wmfe 1							---				45	665	77.9	21.2
Nfe 7							---				45	770	66.0	28.6
Wmfe 4							---				51	798	79.2	23.0
Wmfe 2							---				54	1,240	77.3	21.2
Wfe 1							---				57	1,260	84.0	23.8
Wfe 2							---				57	1,740	80.2	24.8
Nfe 9							---				54	2,310	75.7	25.9
Wfe 3							---				60	3,000	78.0	24.7
Wfe 4							---				60	4,300	72.6	25.5
Ofe							---				60	~6,000	68.0	28.6
Wfe 5							---				66	~14,000	81.5	28.0
Wfe 6							---				63	~16,000	78.4	28.1
Wg 1							---				66	~25,000	70.1	31.9
Ng 10							---				60	~35,000	—	33.8
Wg 3							---				57	~12,000	62.0	34.3
Ng 9							---				51	4,800	68.7	33.0
Sfl 1							---				45	2,500	57.0	35.8
Wg 2							---				51	2,500	61.2	34.2
Safl							---				51	1,920	39.5	36.4
Ng 6							---				51	1,690	74.0	31.6
Ng 5							---				45	1,460	73.0	30.3
Ng 2							---				42	1,130	62.0	32.6
Ng 4							---				42	670	71.7	29.6
Ofl 1							---				36	440	38.0	34.7
Ng 7							---				42	380	69.3	31.6
Ng 3							---				39	315	59.0	33.9
Ng 1							---				45	300	61.0	30.3
Ng 8							---				39	230	68.0	32.2
Sfl 2							---				33	200	42.4	37.6
Wfl 1							---				33	151	46.0	36.2
Ofl 2							---				30	95	42.0	35.6
Wfl 2							---				15	11	—	36.0
Ofl 3							---				7	6	—	37.5

the test itself have mitigated against its wide adoption.

Porter¹⁵¹ apparently devised the first orifice method for measuring the extrusion properties of softened, heated coal under applied pressure. The test also permitted determinations of the softening behavior of the coal by the dilatometer principle, of the maximum expansion pressure after 10 percent free expansion of the coal had occurred, and of the loss in weight of the sample at 1,050° F (566° C). Figure 7 illustrates the apparatus.

Nine American coals (8 from the United States and 1 from Canada), ranging in volatile-matter content from 16.0 to 35.6 percent (as-determined basis), were tested in an atmosphere of preheated nitrogen. Fulton Seam coal (16.0 percent volatile) from Huntingdon County, Pa., showed no extrusion but a maximum expansion pressure of 2 pounds per square inch, whereas Sewell Seam coal (20.2 percent volatile) from Fayette County, W. Va., showed neither extrusion nor expansion pressure. Lower Kittanning ("B") Seam coal (22.0 percent volatile) from Cambria County, Pa., gave an extrusion of 3.5 percent all through the orifice and a maximum expansion pressure of 14.5 pounds per square inch, indicating that this coal was not fluid enough when plastic to have the expansion pressure much relieved by the orifice. Lower Freeport ("D") Seam coal (25.5 percent volatile matter) from Cambria County, Pa., showed an extrusion through the orifice of 60.5 percent, a total extrusion of 65.0, and a maximum expansion pressure of 5.5 pounds per square inch, whereas Upper Freeport Seam coal (29.0 percent volatile) from Indiana County, Pa., gave corresponding extrusions of 55.0 and 75.0

percent and a maximum expansion pressure of 10.0 pounds per square inch.

The greater degrees of fluidity developed by the Freeport coals, compared with the Kittanning coal, by extrusion through the orifice and notches in the piston head, helped relieve the maximum expansion pressure developed. Pittsburgh Seam coal (32.5 percent volatile matter) from Westmoreland County, Pa., gave an extrusion of 65.0 percent all through the orifice and a maximum expansion pressure of 2.0 pounds per square inch. A second Pittsburgh Seam coal (35.5 percent volatile) showed much less fluidity without developing any higher expansion pressure; it gave 31 percent extrusion all through the orifice and a maximum expansion pressure of 2.0 pounds per square inch. Dominion coal (34.5 percent volatile) from Nova Scotia, Canada, although containing more volatile matter than the Pittsburgh Seam coal from Westmoreland County, Pa., and less volatile matter than the Pittsburgh Seam coal from Allegheny County, Pa., showed less fluidity than either. It showed 2.5 percent extrusion all through the orifice, but the same maximum expansion pressure of 2.0 pounds per square inch. Coal from Franklin County, Ill., containing 35.6 percent volatile matter, showed not only no extrusion through the orifice but also no well-defined softening point and no clogging of the gas passage by sintering together of the coal particles.

The relationship of the data obtained to underfeed-stoker, coke-oven, gas-producer, and water-gas-generator operations was discussed, and a provisional scheme was suggested for the classification of coals according to their softening characteristics.

In a later article¹⁵² Porter stated that the comparisons of the data obtained in

¹⁵¹ Porter, H. C., *Proc. 3rd. Intern. Conf. Bituminous Coal*, **1**, 613-30 (1931).

¹⁵² Porter, H. C., *Ind. Eng. Chem.*, **27**, 962-6 (1935).

his earlier investigation "were not strictly quantitative, since it was found necessary in nearly all cases to add to the piston load in varying amount and for different lengths of time in order to retain the charge in the

heated zone. The extrusion was thus, in these cases, influenced during a fraction of the plastic period by the added pressure due to swelling." Some of the earlier data were retabulated, together with the added

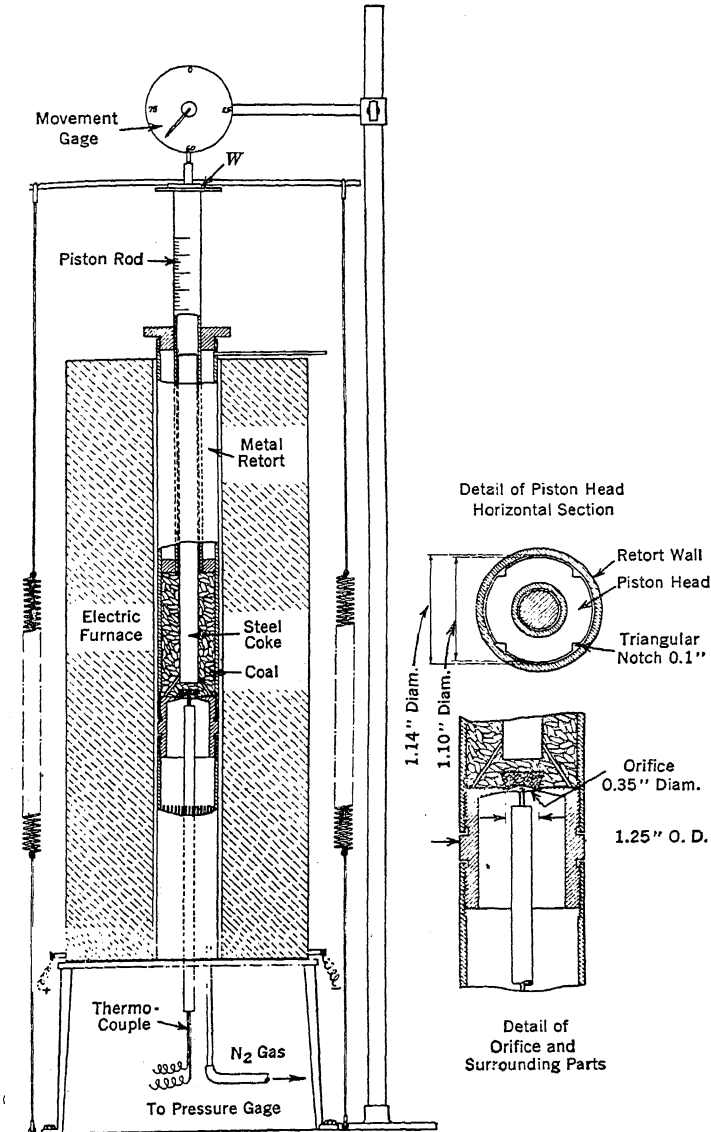


FIG. 7. Apparatus for determining extrusion of softened coal.¹⁵¹

load in pounds and the percentage of the plastic period during which this added load was applied. The Pittsburgh Seam coal from Westmoreland County, Pa., in another test, using a higher piston load continuously applied, was almost completely liquefied, 95 to 97 percent being extruded. Porter pointed out that the difference in the amounts of extrusion shown by the two Pittsburgh Seam coals might be attributed to the higher oxygen content of the coal from Allegheny County, Pa., as compared with that of the coal from Westmoreland County, Pa.

With the object of making the fluidity of the coal itself, so far as possible, the chief factor in the observed results, Porter developed a new extrusion test in which the extent of penetration of the softened coal into an adjoining layer of sized coke particles was determined. No external pressure was applied, the flow of coal being actuated only by gravity and by its own swelling. After charging, the metal capsule was suspended in an inert atmosphere (nitrogen or city gas) and heated at a rate of about 3° C per minute over the temperature range between 400 and 520° C.

Five of the coals studied in the earlier investigation were again tested. The results indicated that the differences in fluidity of the coals was more or less of the same order as found previously, but that the coals of low fluidity, such as the Lower Kittanning from Cambria County, Pa., may swell so strongly, by virtue of retaining expanding gas bubbles in the plastic mass, that they are thereby driven to a greater distance of penetration into the coke layer than a more fluid coal, such as Pittsburgh Seam coal from Allegheny County, Pa., which has a lower swelling pressure. The method gave some indication of the relative penetrating powers of the softened coals, impelled by their own

swelling pressures. It failed, however, to eliminate satisfactorily the uncertain pressure factor that complicates the measurement of fluidity. The extrusion methods described by Porter indicate differences in coals in the combined effect of fluidity and swelling pressure.

Gieseler¹¹⁰ attempted to press softened, heated coal through a nozzle on the lower end of a vertical metal tube. This tube was encased in a glass tube of larger diameter, which, in turn, was surrounded by one of still larger diameter that contained a salt bath for heating. Finely pulverized coal was placed in the metal tube, and the assembly was heated at a rate of 3° C per minute. A tightly fitting piston, whose lower end contained the hot junction of a thermocouple for measuring temperatures, pushed the softened coal through a nozzle of the metal tube and into the inner glass tube. On account of the deposition of tarry constituents on the walls of the metal tube, the piston always stuck after a short period of operation.

An extrusion apparatus, designed by Lum and Curtis,¹³⁷ was used to test 6 American coals. The lowest-ranking coal, Black Creek Seam (39.1 percent volatile matter, dry basis) from Alabama, was not plastic enough to be extruded. The highest-ranking coal, B or Lower Kittanning Seam (17.5 percent volatile matter, dry basis) from Pennsylvania, developed plasticity only to a small degree, and had to be tested under a high pressure with very rapid preliminary heating and with a 0.313-inch-diameter orifice to effect its extrusion. The number of grams of coal extruded through the orifice per minute was defined as "extrusivity"; it amounted to 1.15 grams per minute at a test temperature of 500° C. Formation of hard coke prevented complete extrusion of the charge.

The other 4 coals were tested at several

temperatures and under a standard pressure. In each series of tests with each coal the temperature at the start of extrusion was increased for the successive tests by intervals of 10° C until the entire temperature range of plasticity of the coal had been covered. A second Lower Kittanning Seam coal (22.3 percent volatile matter, dry basis) from Pennsylvania, tested at 430, 440, and 450° C using a 0.156-inch-diameter orifice, gave "extrusivity" values of 0.38, 0.59, and 0.37, respectively. Imboden Seam coal (34.0 percent volatile matter, dry basis) from Virginia, at temperatures of 410, 420, and 430° C, with the same orifice, gave extrusivity values of 0.62, 1.20, and 1.05, respectively, and at 420° C with a 0.0938-inch-diameter orifice, a value of 0.48 gram per minute. Pittsburgh Seam coal (34.8 percent volatile matter, dry basis) from Pennsylvania at 410, 420, and 430° C, with the 0.0938-inch-diameter orifice, gave values of 0.85, 1.17, and 0.75 gram per minute, respectively. No. 2 Gas Seam coal (36.1 percent volatile matter, dry basis) from West Virginia at 410, 420, 430, and 440° C, with the same orifice, gave extrusivities of 0.55, 0.90, 1.59, and 0.80, respectively.

Formation of hard coke prevented the complete extrusion of the coal charge with the Lower Kittanning, Pittsburgh, and No. 2 Gas Seam coals at their highest test temperatures. The relative rate of extrusion through the 0.156- and the 0.0938-inch-diameter orifices by the Imboden Seam coal at its temperature of maximum plasticity, 420° C, was 1.20 to 0.48, or 1 to 0.4. Using the factor of 0.4, the experimental value of the extrusivity, 0.59 gram per minute for the 22.3 percent volatile matter Lower Kittanning Seam coal with the 0.156-inch-diameter orifice, becomes 0.24 gram per minute with the 0.0938-inch-diameter orifice.

When the 4 coals, No. 2 Gas, Pittsburgh,

Imboden, and Lower Kittanning, are arranged in the order of decreasing dry volatile matter content, that is, 36.1, 34.8, 34.0, and 22.3 percent, respectively, their extrusivities, 1.59, 1.17, 0.48, and 0.24 gram per minute, respectively, at their maximum temperatures (430, 420, 420, and 440° C) also fall in the order of decreasing values. Table V in the article by Lum and Curtis indicated that the Imboden Seam coal contained 36.1 percent volatile matter, which placed this coal between the No. 2 Gas coal and the Pittsburgh coal, and then the extrusivities fell out of line. Their Table II, however, showed that the Imboden coal contained 34.0 percent volatile matter, which value was correct according to a private communication from Dr. Lum.

The data obtained by Lum and Curtis showed that the temperatures of maximum pressure for the above-described coals in their gas-flow tests, carried out as described on page 219, were usually lower than the temperatures at which maximum extrusion occurred. Some investigators have stated that the maximum pressure in the gas-flow tests represents the end of plasticity and the beginning of coke formation. To insure that comparable temperature measurements were made in the gas-flow and extrusion tests, Lum and Curtis modified the extrusion apparatus so that both tests could be carried out in the same apparatus. The coal fusion cylinder was wrapped with a brass tubing to serve as a preheating coil for the nitrogen gas, and the lower end of the coil was fitted tightly into the orifice below the coal charge. Gas-flow tests carried out according to the usual procedure, followed by extrusion tests in the same apparatus, showed clearly that coals are in a plastic condition at temperatures higher than that of the maximum pressure in the gas-flow tests. Extrusion of the coal sample could always be made after the tem-

perature of maximum pressure was reached.

Measurements of the fluidity of the plastic layer itself have been made by Sapozhnikov and Finkelstein.^{153, 154, 155} Since their data were explained in terms of relation to those from other "plastometric investigations," the review of these measurements will be given in a later discussion of plastometric investigations of Russian (U.S.S.R.) coals.

SWELLING PRESSURE OR EXPANSION PRESSURE METHODS

Much confusion has resulted from loose and interchanged usage of the terms "swelling" and "expansion" as applied to the act or process of increasing the volume of a coal charge by heating and to the state of the carbonized product resulting from the heat treatment. In some instances, only a linear change, usually in the vertical direction, of the original dimensions of the confined, heated, coal charge is intended; in others, the concept of an increase in pressure within the charge is denoted. The extent of "free" swelling, when no load is applied to the top of a confined, heated, coal charge, may be quite different from the vertical displacement observed when the coal charge is heated under an added load. Some coals may swell even more under load than when no load is applied. This apparent anomaly is explained by the fact that when the charge is under load a portion of the distillation gases and vapors is prevented from escaping and the resulting pressure causes the observed increase in volume. If the load applied is large enough, the coal may be prevented entirely

from increasing in volume, and considerable pressure may be built up.

Worthwhile distinctions made by Damm^{3, 4} were that swelling (*Blähen*) signified a volume change that takes place during the heating of many coals under conditions such that the softened coal can expand freely in a direction perpendicular to the heating surface, whereas force (*Treiben*) denoted the pressure that the softened coal mass frequently exerts when it is obstructed from free expansion. The magnitude of the degree of swelling (*Blähgrad*) is expressed numerically in convenient linear units or as a percentage of the original coal volume, whereas swelling pressure or expansion pressure or, more recently, "driving pressure"⁵ (*Treibdruck*), is usually given in some pressure unit per unit area, such as kilograms per square centimeter or pounds per square inch. Practically, for the coke plant, swelling scarcely comes into account, because the coke oven is confined, and free expansion, except for a limited amount at the top of the charge, is prevented. The possibility of the coal expanding into the free space above the charge is small because most of the swelling is exerted perpendicularly to the heated walls and radiation of heat from the top of the oven is too small to affect a very deep layer of the coal charge.

Investigations have shown repeatedly that a strongly swelling coal often develops a high expansion pressure. On the other hand, it is entirely possible that a feebly swelling coal may show high expansion pressure, and, conversely, that a strongly swelling coal may develop no expansion pressure. In practice, therefore, expansion pressure has become associated with those coals that show a deficient after-shrinkage. This property expresses itself by scaffolding of the coke in the oven or by its sticking on the walls, so that the

¹⁵³ Sapozhnikov, L. M., and Finkelstein, P. K., *Khim. Tverdogo Topliva*, 6, No. 1, 34-40 (1935).

¹⁵⁴ Sapozhnikov, L. M., *Coal Carbonisation*, 3, 42-4, 95-7, 145 (1937).

¹⁵⁵ Sapozhnikov, L. M., *Coke and Smokeless-Fuel Age*, 1, 27-9, 58-60, 131 (1939).

coke is difficult to push from the oven chamber. For coke-oven practice, coals which show a so-called transient pressure are especially dangerous to use. After coking such coals, the coke formed is found to have shrunk enough during the coking process so that it can be easily pushed from the oven, yet because of a high expansion pressure that is developed at some stage in the coking process the oven walls and buckstays have been strongly deformed. Continued use of such coals in a coke oven usually results in pushing difficulties because of the penetration of coke into the bulges in the coke-oven walls.

The definitions given by Damm have contributed much to clarify the terms used to express the data obtained in both laboratory and larger-scale, in some instances full-size, coke-oven tests designed to determine changes in volume and in pressure of the coal during its carbonization. However, the loose and interchanged use of the terms "swelling" (*Blähen*), "force" (*Treiben*), "degree of swelling" (*Blähgrad*), and "expansion pressure" (*Treibdruck*) made by earlier investigators has persisted to some extent, even to the present. It is hoped that the necessity for satisfactory definitions, improved methods of measurements, and correct interpretations of test data on the "plasticity" and expansion properties of coal and coal blends under the conditions of industrial carbonization and combustion, long since recognized and under extensive study by many coal investigators, will ultimately lead to standardized practices. Progress in this direction is being made by Subcommittee XV on Plasticity and Swelling of Coal of Committee D-5 on Coal and Coke of the American Society for Testing Materials.¹⁵⁶

The important problem of how a coke-

oven operator can assure himself that the coal or coal blend he is using or may be called upon to test or use will not expand during its coking to such an extent that it will cause damage to a commercial coke oven is best answered by tests in the oven itself. However, such a procedure is risky and likely to result in large financial loss if the coal has dangerous expansion properties. The solution of the problem appears to lie in large-scale tests made in movable-wall ovens, preferably heated from both sides. The elaborate equipment required and the cost of materials and of carrying out such tests have minimized their application. Empirical indications, from which predictions can often be made with a fair degree of certainty as to the safe or harmless expansion pressures to be expected in the commercial coke oven, when using a given coal or coal blend, have been obtained from the results of many smaller-scale tests. The "laboratory methods," using charges of 1 to 120 grams, and small test ovens, using 4 to 400 pounds of coal, have given results of great value in predicting the behavior of a coal or coal blend in the coke oven itself or under test conditions that correspond to those of actual operation.

All expansion pressure tests are designed for unidirectional heating and either allow the charge to expand under "constant pressure" or under "constant volume." The latter designation is not strictly accurate as the coal is usually permitted to expand the limited amount which is considered safe for industrial practice, after which pressure is applied to maintain the volume constant during the rest of the test. In both types of tests the coal charge is loaded. In the first, the charge moves against the applied force and the volume increase is measured; in the second, the applied force is large

¹⁵⁶ *Proc. Am. Soc. Testing Materials*, **38**, Pt. I, 410-11 (1938), **39**, 434 (1939), **40**, 339 (1940).

enough to prevent expansion of the charge (beyond a certain limit).

The methods of determining the swelling pressure or expansion pressure of coals are numerous and range from laboratory tests taking as little as 1 gram of coal to full-scale, commercial coke ovens taking several tons of coal. A rigid classification that distinctly divides the different methods according to comparable size apparatus and test procedures without some overlapping is difficult. For convenience, the methods have been somewhat arbitrarily subdivided as follows:

1. Laboratory methods (coal charges of 1 to 120 grams).
 - (a) Constant-pressure type.
 - (b) Constant-volume type.
2. Larger-scale swelling test apparatus or small experimental test ovens (coal charges of 4 to several hundred pounds).
3. Measurement of distortion of coke-oven walls under pressure.
4. Expansion pressure measurements in coke ovens.
5. Large-scale research installations, two-sided heating.
6. Carbonization of coals under high applied pressure (low-rank coals).

LABORATORY TEST METHODS

Constant-Pressure Type of Apparatus. In 1920, Korten¹⁵⁷ pointed out the possible danger of carbonizing expanding coals in a coke oven. Recognizing defects in earlier laboratory test methods, he endeavored to reproduce so far as possible practical operating conditions in his laboratory apparatus. A coal charge of 100 grams was coked in a vertical, thick-walled, cylindrical, iron crucible under standard conditions in a gas-fired furnace. The bottom end of a piston, perforated to permit escape of gases, rested on the coal charge. The piston rod projected through the cover

of the crucible and supported a weighted lever at the top. The shorter arm of this lever was fixed; the longer, weighted arm moved in accordance with the vertical displacement of the piston during the coking of the coal. This movement, magnified by the ratio of the lengths of the two lever arms, was traced on a paper-covered revolving drum. Adjustable weights, placed on the longer lever arm, permitted the load to be altered as desired for individual tests.

Laboratory results obtained on two coals agreed with their coking behavior in coke-oven practice. One coal, containing 27 percent volatile matter (basis not stated), showed a contraction of 4 percent in the test apparatus and was known to be easily coked and pushed from the coke oven. The second coal, containing 14 percent volatile matter (basis not stated), expanded nearly 6 percent during carbonization, remained expanded 3.5 percent at the end of the laboratory test, and was known to push only with difficulty and with damage to the oven walls. Using an unloaded lever, Korten also determined the magnitude of "swelling." Curves comparing these data with those obtained when a weighted lever was used showed the relationship between "swelling" and "expansive power" of the two coals.

The test method of Korten has been developed further in two general directions: (1) the constant-pressure method, in which the load on the coal charge is maintained constant and the volume of the coal allowed to change; and (2) the constant-volume method, in which the volume of the coal is kept constant by corresponding suitable variations of the applied load. Both methods have undergone many minor changes in their working principles and have been extended to larger-scale test practices, particularly since 1928.

¹⁵⁷ Korten, F., *Glückauf*, **56**, 652-5 (1920); *Stahl u. Eisen*, **40**, 1105-8 (1920).

Apparently, the first constant-pressure test method, based upon the earlier test method of Korten, was developed in Germany some years before its first published description appeared in 1930. The method was designated as the "Koppers A.-G. 'laboratory method,'" ¹⁵⁸ which has distinguished it from the larger-scale test methods later developed by the same company. The method was characterized by the use of a "constant load," usually 1 kilogram per square centimeter, on the top surface of the coal charge throughout the 4-hour test. Other descriptions of the apparatus and test procedure have appeared, ^{59, 61, 62, 159, 160, 161} Foxwell gave 1.165 and Mott and Spooner gave 1.16 kilograms per square centimeter as the pressure applied to the coal charge.

The coal container was an iron or steel crucible with a replaceable sieve bottom. The crucible was lined on the inside and bottom with asbestos, and was charged with 80 grams of minus 1.0-millimeter air-dried coal. The charge was compressed to a chosen fixed height to give a corresponding desired standard bulk density, and was then covered with asbestos. A sillimanite disk and a steel piston, each containing four vertically aligned holes to permit escape of gases and vapors from the top of the charge, were placed on the asbestos-wrapped charge. The top end of the piston rod supported a lever at a point whose distance from the fulcrum of the lever was one-third that from the fulcrum to the point of suspension of the applied load. With this translation ratio of 3 to 1 and

a 10-kilogram loading weight the effective load on the coal charge was stated to be 1 kilogram per square centimeter. Provision was made also to use smaller weights, so that the load on the charge could be varied in steps of 0.2 kilogram per square centimeter. The longer arm of the lever carried a recording pen that registered on a rotating drum the vertical movement of the coal charge during the 4-hour test. The charge was heated by a standardized gas flame in a furnace that was claimed to give only unidirectional heating at the bottom of the crucible. Gases and vapors distilling from the coal charge through the perforated bottom of the crucible and combustion gases from the burner escaped through four or eight openings in the firebrick ring below the crucible.

Coals that showed some or much expansion during the first hour or two of the 4-hour test period and little aftershrinkage were considered dangerous for coke-oven practice. Comparative results obtained in plant operation on the same coals over a period of years allowed the coals to be broadly grouped and correlated for coking purposes. Expansion curves based on a charge density of 750 kilograms per cubic meter or 46.8 pounds per cubic foot (dry-coal basis), showing millimeters of indicator movement plotted as ordinates against hours of heating as abscissas, were applicable to plant practice: (1) Coals whose curves rose *above the zero line* and finished in space *a* (0 to -4 millimeters) were considered *very dangerous*; in *b* (-4 to -8 millimeters), *dangerous*; and in *c* (more than -8 millimeters), *possibly dangerous (transient expansion)*. (2) Coals whose curves *did not rise above the zero line* and finished in space *a* were considered *dangerous*; in *b*, *possibly dangerous*; and in *c*, *harmless*. Only coals of

¹⁵⁸ H. Koppers A.-G., *Koppers Mitt.*, **12**, No. 1, 1-23 (1930).

¹⁵⁹ Heuser, P., thesis, Technische Hochschule, Aachen, 1930, 55 pp. typed.

¹⁶⁰ Foxwell, G. E., *J. Inst. Fuel*, **12**, 281-300 (1939); *Gas World*, **111**, *Coking Sect.*, 118-23, 129-31, 141-2 (1939).

¹⁶¹ Mott, R. A., and Spooner, C. E., *Fuel*, **18**, 329-44, 371-9 (1939).

type 2c can be stamp-charged with safety. Figure 8, for example, represents coal types 1a, 2b, and 2c.

This method of determining expansion did not simulate coke-oven practice in one important respect, namely, the coal throughout the test was under a constant load, which normally was greater than the

were sometimes misleading, and an exact comparison of expansion pressures on different coals could not always be made. The method has served qualitatively, however, as a very useful guide when parallel data were available on the same coals when coked in commercial ovens. The method possessed the advantage over constant-vol-

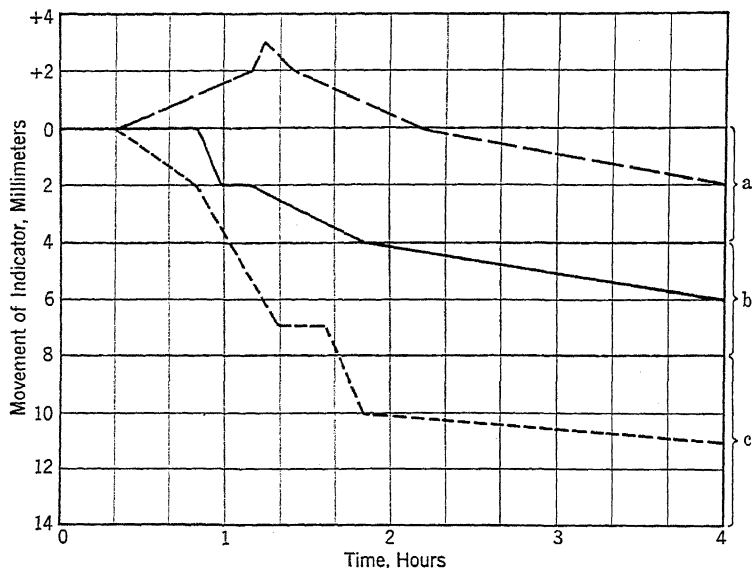


FIG. 8. Curves for coals of different expansion characteristics.¹⁵⁸

expansion pressure of the coal. At the outset this load increased the bulk density of the coal as charged; the extent of increased compression varied with different coals. During the test, the pressure of the load caused the curve for a noncaking coal to fall very little, as this kind of coal did not soften and hence the diminution was due solely to degasification. On the other hand, for a caking coal whose decomposition during its softening period was increased by pressure, the curve fell quite markedly. The shrinkages indicated by the heights of the projected curves obtained by the above method, therefore,

were sometimes misleading, and an exact comparison of expansion pressures on different coals could not always be made.

The method has served qualitatively, however, as a very useful guide when parallel data were available on the same coals when coked in commercial ovens. The method possessed the advantage over constant-vol-

ume methods of requiring only 20 minutes to get the test started, after which very little supervision was needed.

Swietoslawski, Roga, and Chorazy¹²⁰ used the method of Korten and an apparatus constructed by H. Koppers. The vertical displacement of the loaded piston resting on the coal charge was registered through a lever system on a revolving drum, on which a curve of swelling and contraction was obtained. The heated coal was kept under a constant pressure of 0.2 kilogram per square centimeter. The data obtained were not recorded but apparently were used in evaluating the briquetting

properties of slacks from anthracite and various kinds of bituminous coals.

Roga¹⁶² measured the expansion pressure of coal by the Korten-Koppers A.-G. method; he stated that expansion pressure depended on the plastic state of the coal developed during heating and on the nature of the nonmelting and melting substances; which varied both quantitatively and qualitatively for different coals. He believed, also, that contraction occurred in the "third" stage of coking and depended on the amount of degasification. Besides the ability to cake and become plastic a good coking coal had to possess also a certain expansion pressure because it made possible better saturation of the nonmelting constituents. The course of gas evolution and the thermostability of substances responsible for caking also were very important. Caking gas coals were unsuited for coke production owing to the complete absence of expansion pressure, which made impossible sufficient impregnation of the whole mass of coal in the oven.

Šimek and Coufalík¹⁶⁷ used the Koppers A.-G. laboratory apparatus¹⁵⁸ to measure the expansion pressure of three petrographic constituents—fusain, durain, and clarain—of an Ostrau-Karwin coal. Shrinking of the constituents was observed to increase slightly in the order named. All expansion curves, when projected as in the Koppers A.-G. method, ended in the region *b*. The use of the "improved" apparatus of Pavlíček and Panuš¹⁶³ gave similar results. Šimek and Coufalík concluded that no one of the petrographic constituents of the coal alone had a pronounced expansion power.

Kircher¹⁶⁴ determined the expansion pressure of 9 German coals and the after-shrinkage of their semicokes. The 80-millimeter-diameter crucible was charged loosely with 100 grams of air-dried coal (50 to 60 percent under 2 millimeters, or 60 to 70 percent under 3 millimeters), the piston and piston guide plate put in place, and the assembly set in an electric furnace preheated to 900°C. The dynamometer spring was set to a tension of 4 kilograms by means of a set screw on the longer arm of the lever. The relative lengths (80 and 480 millimeters) of the lever arms gave a translation ratio of 1 to 6, and an effective pressure on the top surface of the coal of around 0.5 kilogram per square centimeter (compared to about 1 kilogram per square centimeter in the "laboratory method"). The expansion pressure curve was recorded automatically on a revolving drum.

Coals tested included samples from Viktoria, Matthias, Gretchen, Wasserfall, Sonnenschein, Girondelle, Finefrau Nbk., Finefrau, and Mausegatt Seams, containing 31.2, 29.3, 22.5, 19.3, 19.6, 17.4, 15.5, 16.3, and 14.7 percent of volatile matter [pure-coal basis], respectively. The first 4, higher-volatile (lower-rank), coals showed very little expansion pressure, but appreciable shrinkages of their semicokes. Beginning with the Sonnenschein Seam coal a strong expansion pressure was developed, which attained its maximum in the Finefrau Seam coal, whereas the Mausegatt Seam coal showed a small shrinkage. The data were related to results obtained on these coals in commercial coke ovens.

The Koppers A.-G. "laboratory method"¹⁵⁸ was used by Mott and Spooner¹⁶¹ under their own designation of "Koppers small-scale swelling test" or "old standard

¹⁶² Roga, B., *Przemysl Chem.*, **15**, 314–6, 329–32 (1931); *Chem. Abs.*, **26**, 2570–1 (1932).

¹⁶³ Pavlíček, F., and Panuš, K., *Hornický Věstník*, **16**, 166 (1934).

¹⁶⁴ Kircher, A., *Glückauf*, **74**, 725–32, 750–6 (1938).

test." In a later paper,¹⁶⁵ Mott said that the equipment was the standard used in Germany. However, Mott and Spooner¹⁶¹ stated, "The magnification of the movement of the plunger is 3.6/1. A weight is hung from the arm to give a pressure on the coal of 1.16 kilograms per square centimeter (16.5 pounds per square inch)."

results of temperature measurements at points near the top and bottom of the charge, were developed to increase the temperature of the charge. Changes in the size of coal and pressure applied also were introduced. The construction features and test conditions in the three test methods are summarized in Table III.

TABLE III
SUMMARY OF CONDITIONS USED BY MOTT AND SPOONER

	Old Standard	(Ordinary Firebrick) Modified Test 2	(Insulating Firebrick) Modified Test 3
Upper furnace firebrick	Ordinary	Ordinary	Insulating
Lower furnace firebrick	Ordinary	Insulating	Insulating
Waste gas offtakes in lower firebrick	4	8	8
Weight of coal, grams	80	80	80
Size of coal, I. M. M. mesh	-10	10-20	10-20
Dry bulk density, kg/cu m	750	750	750
Pressure, kg/sq cm	1.16	1.16	0.5
Rate of heating			
Bottom of charge, °C/min	6.7	25	33
Top of charge, °C/min	0.5 *	4.5	9
Temperature of charge			
1 mm from bottom, °C	600	850	940
1 mm from top, °C	400	440	750
Time of test, hours	4	2	2

* Over range of 400 to 430° C only.

These values differ from the more usual values of a magnification of 3 to 1 and a pressure of 1.0 kilogram per square centimeter (in one case,¹⁶⁰ 1.165 kilograms per square centimeter) given in earlier descriptions of the apparatus.^{59, 61, 62, 158, 159, 160}

Mott and Spooner¹⁶¹ believed that temperatures reached during the test in the Koppers A.-G. "laboratory method"¹⁵⁸ were too low to obtain reliable information on the shrinking properties of the coke produced. Two modifications, in construction of the "old standard test," based upon

Under the test conditions in "old standard test 1" the coal did not pass completely through the plastic range (assumed to be 400 to 500° C) at the top of the charge, despite the fact that the test was prolonged for 4 hours. In modified test 3 a temperature of 720° C was obtained at the top of the charge after 2 hours. Beyond this the temperature rose slightly, but the reactions were substantially complete after 2 hours, which time, therefore, was taken, as the test period.

Comparison of results obtained on the same coals by the three test methods showed that the use of sized (10- to 20-

mesh) coal in the two modified test methods gave less expansion than resulted from the use of minus 10-mesh coal in the old standard test. Mott and Spooner concluded that "the use of coal of 10- to 20-mesh size would not alter the petrographic characteristics of a coal in such a way as to give a misleading result." They based this conclusion upon experiments made on three mixtures of bright coal and durain. Durain was determined by their own method.¹⁶⁶ Both constituents, originally of $\frac{1}{2}$ - to $\frac{1}{4}$ -inch size, were crushed to pass 10 mesh, and then sieved into "under 10," "10 to 20," and "under 20" mesh fractions. The percentages of durain in the several fractions did not differ greatly from the amounts contained in the original starting mixtures. The first mixture, containing 10 percent of durain originally, showed 12, 10, and 12 percent of durain in the "under 10," "10 to 20," and "under 20" mesh fractions, respectively. The second mixture (20 percent durain) gave 23 percent of durain in each of the three fractions. The third mixture (30 percent durain) showed 28, 34, and 24 percent of durain in the "under 10," "10 to 20," and "under 20" mesh fractions, respectively.

Mott and Spooner concluded that, since only a few coals contain more and most coals usually contain much less than 25 percent of durain, it is unlikely that coals which are dangerous to oven walls would contain much durain. Furthermore, the use of 10- to 20-mesh coal would omit all the fusain and thereby tend to make the coal appear slightly more dangerous than the total coal actually would be, thus giving a small factor of safety to which no one would object in expansion studies.

Presumably, the initial ($\frac{1}{2}$ - to $\frac{1}{4}$ -inch) sizes of the bright coal and durain in the

mixtures used by Mott and Spooner represented all the original bright coal and durain. Otherwise, the mixtures would not be representative of the two starting constituents, since bright coal, especially, is often very friable. Moreover, the rejection of coal under 20 mesh in modified tests 2 and 3 might well eliminate some strongly swelling, bright coal, thus making the sample nonrepresentative, and at the same time reduce the swelling observed, giving consequently an erroneous conclusion of the dangerous or safe character of the sample, particularly when borderline coals are tested. It seems safer practice to include all the coal, as is done in most experimental methods and in commercial practice.

It is not clear just what factor was used in calculating the expansions and contractions observed in millimeters to the percentage basis. Mott and Spooner¹⁶¹ stated that "the swelling and contraction recorded in millimeters may be corrected to a percentage basis by dividing by 1.27." This statement referred to the data of their Table III¹⁶¹ and to other data reported throughout their paper for tests using a bulk density of 750 kilograms per cubic meter (46.8 pounds per cubic foot) dry basis and a height of 37.5 millimeters for the coal charge.¹⁶¹ It is not clear how this factor of 1.27 was derived. Mott and Spooner¹⁶¹ cited "a Durham coal which in the standard test gave an expansion of 15 millimeters (11.1 percent.)" This percentage value would result from a calculation using a 3.6 magnification of the movement of the plunger and a height of 37.5 millimeters for the coal charge. Thus, 15 millimeters \times 100/(3.6 \times 37.5) millimeters equals 11.1 percent. However, the factor here is 100/(3.6 \times 37.5), or 1.35, and not 1.27. Which factor, 1.27 or 1.35, was actually used by Mott and Spooner could not

¹⁶⁶ Spooner, C. E., and Mott, R. A., *Fuel*, **16**, 96-106 (1937).

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be established. Percentages calculated from recorded millimeters of expansion and contraction, using either factor, do not check with percentages recorded for the same test elsewhere in their paper. It is unfortunate that such discrepancies occur, because much of the value of comparative test data is thereby lost. However, regardless of which factor was used in individual cases, the percentages of swelling and contraction reported by the three test methods would be fairly relative to each other, and, assuming the correctness of the reported value in millimeters, would not be far out of line.

Mott and Spooner determined the expansion characteristics of 42 different coals by one or more of the three test methods just described. Results by the three methods did not always lead to the same conclusion as to the degree of safe or dangerous expansion of an individual coal. Ten coals suspected of being dangerous under certain conditions and 3 coals known to have caused damage to oven walls in coke-plant operation were therefore tested also by at least two other widely used methods. The data obtained by Mott and Spooner by six different test methods, and those obtained by the U. S. Bureau of Mines on 4 of the same coals, will be summarized and discussed later in the section "Comparison of Expansion Pressure Test Methods and Results" (see page 305).

A modified Koppers "constant-pressure" test method apparently has been used in most of the investigations of the swelling properties of Russian (U.S.S.R.) coals. Descriptions of the test method have been published in Russian^{167, 168} and in Eng-

lish.^{154, 155} Except for possibly the first investigation, the apparatus was modified to permit simultaneous measurements of the thickness of the plastic layer along with the linear expansion and aftershrinkage (termed "final drop" or "final settling" of the coke) of the coal charge during carbonization. The developed test method was called the "plastometric investigation." Since most of the tests with the apparatus have emphasized data for special properties of the plastic layer of the coal charge, the test method will be described separately in a later section of this chapter (see page 280).

Comparative studies of the constant-pressure Koppers A.-G. laboratory method and constant-volume test methods have been made by Baum and Heuser^{159, 61} and by Lambris.^{99, 169} For convenience, the results of these studies will be summarized in the following section.

Constant-Volume Type of Apparatus. This method differs from the constant-pressure type in that the external load applied to the coal is so regulated that the charge cannot expand beyond its original volume (or beyond some defined limit) during the test period. The loading pressure, therefore, always opposes the expansion pressure developed by the coal. Usually, the constantly held volume of the charge is recorded as a straight horizontal line, and the expansion pressure by a curve on the same or separate revolving drums.

Damm³ modified the Korten (constant-pressure) test method so that the coal charge was maintained at a constant volume, that is, never exceeding its original volume during the test. The maximum load required to accomplish this, expressed in kilograms per square centimeter pressure applied to the top surface of the coal

¹⁶⁷ Sapozhnikov, L. M., *Domez*, 1931, No. 6, 46-62.

¹⁶⁸ Sapozhnikov, L. M., and Bazilevich, L. P., *Khim. Tverdogo Topliva*, 3, Nos. 2-3, 79-102 (1932).

¹⁶⁹ Lambris, G., *Gas- u. Wasserfach*, 76, 1-3 (1933).

charge, was defined as the expansion pressure (*Treibdruck*) of the coal. The ratio of the original to the final height of the charge, expressed in percent, gave the aftershrinkage of the coke.

Swelling curves obtained under no added load and expansion pressure curves determined under loads just sufficient to prevent an increase in the volume of the coal charge were constructed from data obtained on 6 representative German coals from Upper and Lower Silesia and Westphalia. For example, a high-swelling coal under no added load showed about 47 millimeters of free swelling, whereas under a load of 0.4 kilogram per square centimeter, the swelling force was exactly balanced. When the 6 coals were arranged in the order of their increasing expansion pressures, the order, in general, was the same as that of their increasing rank according to carbon content (ash-free basis) but inversely to that of the reactivity of their cokes toward carbon dioxide. The method required constant supervision to make the necessary adjustments in load to keep the volume of the coal charge constant during the test. Even then, some inaccuracies were introduced in the measurements because these adjustments could not be made quite simultaneously with the beginning of changes in the volume of the charge.

Hofmeister⁵² measured quantitatively the magnitude and duration of the expansion pressure and of subsequent shrinkage of a large number of German coals. The coal charge was carbonized under constant volume until shrinkage set in. His method was based on that of Damm³ but showed essential changes. A study of the influence of various factors during coking showed: that the expansion pressure (1) increased in general with increased rate of heating; (2) increased for both dry and moist coals

with increased bulk density, which itself depended on the size and closeness of packing of the coal; (3) decreased at constant bulk density with decrease in particle size of the coal; (4) decreased with additions of moisture up to 5 percent; and (5) decreased with additions of diluents such as coke breeze. The observation that an increased rate of heating or reduction in carbonizing time increased the expansion pressure was criticized by Koppers and Jenkner.⁵⁹ Hofmeister found that the expansion pressures exerted by coal mixtures were not the mean of those of the constituent coals, often departing as much as +150 to -50 percent from the mean value. The cause of expansion pressure was discussed very briefly. Hofmeister considered swelling to have only secondary importance, whereas expansion pressure has an important influence upon coke formation and is not an entirely undesirable property of coal.

Hofmeister claimed the following advantages of his method over that of Damm:³ (1) saving of time; (2) greater accuracy (within 0.01 kilogram per square centimeter or within 2 percent of the expansion pressure value in duplicate tests compared with somewhat less than 0.5 kilogram per square centimeter checks in duplicate tests by Damm's method); (3) lower pressure applied to the coal charge at beginning of test; and (4) good agreement with the data of Damm on the same coals. Hofmeister's test had to be supervised closely during the 3-hour test period. The load was usually first applied after expansion started and was then varied correspondingly to keep the volume of the charge constant.

Pieters¹⁰⁴ determined the swelling pressure of coal under conditions of constant volume. With increased external pressure the coal mass became more compact with

less pore volume, which caused swelling at lower temperatures. Swellings were observed between 360 and 460° C for coking coals; at 650 to 825° C definite shrinkages occurred. Noncaking coals showed no swelling but gradual shrinkage during the whole period of their destructive distillation.

Baum and Heuser^{150, 61} made a careful study of earlier methods for determining the expansion pressure of coal. Of these, they considered the constant-pressure method of Koppers A.-G.¹⁵⁸ and Hofmeister's modification⁶² of the Damm constant-volume method³ worthy of further special studies. Comparative tests of the Koppers and Hofmeister test methods were made by Baum and Heuser with particular regard to whether these methods actually provided strictly unidirectional heating. They found that at any one stage of heating in the Hofmeister method the primary tar was released from the charge in U-shaped layers which moved upward and inward as the heating progressed, whereas in the Koppers method the primary tar was released from layers exactly parallel to the base of the crucible. They concluded that the Hofmeister crucible must have been heated to a certain extent from the side, and, therefore, that the observed expansion pressures were accordingly lower than if the heating had been strictly unidirectional. Baum and Heuser believed, however, that other features of the Hofmeister method were better adapted to true measurements of expansion pressure and, therefore, modified the apparatus in several respects to improve the method of heating and general operating technique.

The inner construction of the electric furnace was changed to allow the progress of coking to proceed exactly parallel to the base of the crucible and in a vertical direction toward the piston, so that the total

expansion pressure acted on the piston head. The data obtained were plotted using load in kilograms per square centimeter as ordinates versus time in hours as abscissas. The values of the ordinates were translated directly into values of the expansion pressures by multiplying by the number of load springs used. The expansion pressure curve for coal I showed a maximum load of 0.3 kilogram per square centimeter, or a maximum expansion pressure of 0.6 kilogram per square centimeter; for coal II a maximum load of plus 0.4 kilogram per square centimeter, or a maximum expansion pressure of 1.29 kilograms per square centimeter; and for coal III a maximum load of 1.1 kilograms per square centimeter, or a maximum expansion pressure of 2.2 kilograms per square centimeter. Coals I and II showed contractions in volume of 5.4 and 2.7 percent, respectively; coal III showed an increase in volume of 5.2 percent.

Tests were made also in the Koppers A.-G. constant-pressure apparatus.¹⁵⁸ The data were plotted using movement of the pointer in millimeters as ordinates versus time in hours as abscissas. Coal I was adjudged to be nonswelling, markedly contracting, and, at normal bulk density, absolutely harmless, a conclusion that was confirmed by experience. Coal II was found to be strongly swelling temporarily, but possessing sufficient aftershrinkage. Coal III was considered to be an extraordinarily high swelling coal and one that did not shrink. The increase in volume here was about 10.4 as against only 5.2 percent in the modified Hofmeister constant-volume test method. The difference in shrinkage was attributed to the incompleteness of the final evolution of the volatile matter because a temperature of only 450° C was reached in the upper portion of the coal

charge and 650° C in the lower portion in the Koppers A.-G. apparatus.

Comparison tests were made on the same coal by the modified Hofmeister laboratory method and the Koppers A.-G. large-scale oven test⁵⁹ with one movable wall whose movement was transmitted to an oil-pressure cylinder and quantitatively recorded. The expansion pressures found were 2.1 kilograms per square centimeter in the laboratory test and 1.9 kilograms per square centimeter in the large-scale test. This difference was attributed to the fact that "in a test crucible not even the slightest expansion or compression of the coal is possible, and that, therefore, the total expansion pressure is registered," whereas in the oven chamber the coal had a certain possibility of expansion, and, further, that a part of the expansion pressure was lost by compressing the loose coal toward the oven center. [Apparently the authors neglected the thermal expansion of the test cylinder in drawing the above conclusion.]

Baum and Heuser^{159, 61} also investigated the direct influence of various sieve fractions of a dangerously expanding Ruhr coal and of its petrographic constituents on the expansion pressure as determined by the Koppers A.-G. method.¹⁵⁸ The whole coal and its sieve fractions—under 0.2, 0.2 to 0.5, 0.5 to 1.0, 1.0 to 2.0, 2.0 to 4.0, and greater than 4.0 millimeters—were tested. The smallest size gave the greatest decrease in expansion pressure; the next three larger sizes showed much less, but nearly equivalent expansion pressures; the two largest sieve sizes and the whole coal showed still less, although almost identical, expansion pressures. Samples smaller than 1 millimeter were ground from the larger sizes, and all the tests were made at bulk densities of 800 kilograms per cubic meter. It would appear that these samples would not be representative of the coal. The

sieve size of the whole coal was not stated. Presumably, it was under 1.0 millimeter if the Koppers A.-G. method was followed strictly. Suggestions were offered that the fine sizes had undergone more oxidation and that the size under 0.2 millimeter may have contained considerable fusain, since its coking residue appeared to have sintered only slightly. These suggestions would account for the lower expansion pressures observed in the finer sizes than were observed for the larger sizes.

Expansion curves were next determined on the fusain portion of this coal at bulk densities of 750 and 800 kilograms per cubic meter. These tests showed the expansion pressures to be quite independent of the density, and the residues were not in the least sintered and had not shrunk.

The durain (dull) portion of this coal, when tested under like conditions, showed that the charge of 750 kilograms per cubic meter would be harmless, whereas that of 900 kilograms per cubic meter closely approached the dangerous zone.

The vitrain or bright portion of this coal at bulk densities of 750, 800, and 900 kilograms per cubic meter showed high expansion pressures and unsatisfactory shrinkages.

The clarain portion of another coal, tested at bulk densities of 750, 800, and 900 kilograms per cubic meter, showed almost identical expansion curves at the two lower densities and would be judged as harmless. The charge of 900 kilograms per cubic meter, however, developed very dangerous expansion properties and gave but little shrinkage. The results were in keeping with plant practice on this type of coal. The vitrain portion of this coal, tested at the same bulk densities, showed high expansion pressures in all instances and but little shrinkage, indicating a very dangerous coal under all these conditions.

An English coal of high vitrain content, tested at the same bulk densities, though showing similar expansion pressures, had a high degree of shrinkage. The counteraction of this shrinkage upon the expansion would make this coal more satisfactory for oven operation. A Ruhr cannel coal and an English durain (dull coal) were each tested at bulk densities of 750 and 900 kilograms per cubic meter. These coals acted alike; all tests indicated large shrinkage and no expansion. The shrinkages of the 750 kilograms per cubic meter charges were more pronounced with time than those of the 900 kilograms per cubic meter charges.

Lambris⁹⁹ adopted the conceptions of *Blähen* and *Treiben* as defined by Damm.^{3, 4} To study these properties, Lambris investigated 12 coking coals of varying rank from the Rhenish-Westphalian district. The expansion pressures were measured by the Damm constant-volume modification³ of the Korten method¹⁵⁷ and by the Koppers A.-G. constant-pressure method.¹⁵⁸ Bulk densities between 790 and 810 kilograms per cubic meter were used in all tests. Results obtained by the two test methods were in good qualitative agreement. Expansion pressures, measured by the constant-volume method, ranged from zero to 4.80 kilograms per square centimeter. The 1 coal showing zero expansion pressure was strongly infiltrated with splint coal. The 4 coals showing the highest expansion pressures (4.00, 4.31, 4.80, and 4.80 kilograms per square centimeter) were predominantly bright coals, containing but very little splint coal and fusain. These 4 coals also were very strongly expanding by the constant-pressure test method. They supported a total load of 30 kilograms on the coal charge, and, in some instances, were said to raise the lever arm above its "null"

position. Numerical data for this method were given for only 1 coal. The data showed that this coal expanded throughout the test to a maximum of about 1 millimeter above the null line. This coal gave an expansion pressure of 4.80 kilograms per square centimeter by the constant-volume method.

Using well-recognized methods, modified slightly in some instances, Lambris determined also the proximate analyses, coke yield (Bochum method), softening point,⁸ degree of swelling,^{51, 170} caking capacity,¹²² course of degasification,³ plasticity,^{111, 108} pressure extraction with benzene,¹⁷¹ and low-temperature tar yield¹⁷² on the same 12 coals. Except for a rough parallelism between the expansion pressures and the degrees of swelling shown by 8 of the 12 coals, no consistent relationships that could be expressed numerically were found among the results of the several tests. All coals that showed expansion pressures during coking were both swelling and caking; all swelling coals caked; and some strongly caking coals neither swelled nor showed expansion pressures. These relations depended upon the physical and chemical properties of the fused coals. Some coking coals giving virtually the same middle degasifications (between 25° C below and 25° C above the softening point) showed very great differences in caking capacity, degree of swelling, and expansion pressure.

Lambris also studied the stepwise loss of the expansion pressure, degree of swelling, and agglutinating value properties caused by heating 4 of the coals (2 very strongly expanding and 2 feebly expanding) for

¹⁷⁰ Pieters, H. A. J., *Het Gas*, **49**, 219-21, 310-5, 523-32 (1929).

¹⁷¹ Fischer, F., Broche, H., and Strauch, J., *Brennstoff-Chem.*, **5**, 299-301 (1924), **6**, 33-43 (1925); *Fuel*, **5**, 466-75 (1926).

¹⁷² Fischer, F., *Brennstoff-Chem.*, **2**, 229-37 (1921); *Elektrotech. Z.*, **42**, 809-14 (1921).

prolonged periods of time at 200° C in an atmosphere of nitrogen. The magnitude of the units expressing these properties dropped in the order named, that is, the expansion pressure first fell to zero within 2 to 8 hours, the degree of swelling dropped 10 to 40 percent, and the agglutinating number (Meurice) either rose or fell. With continued heating up to 24 to 48 hours, 3 of the coals lost all their swelling power, and the agglutinating numbers dropped gradually. The results obtained by the preheating treatment were compared with conditions in the commercial coke oven. It was concluded that coals that show the most rapid loss of expansion power by preheating should be considered the least dangerous in a coke oven. In other words, even though a coal shows high initial expansion pressure, if this is reduced early enough in the coking process, no danger to the oven walls should result.

After 3 months' storage of the powdered samples at ordinary temperatures in closed glass vessels from which the air had not been removed previously, each of these same 4 coals was tested for softening temperature, expansion pressure, degree of swelling, and agglutinating number. The softening temperature of each coal was found to have increased 75 to 90° C, which corresponded with the temperature of maximum plasticity by the Foxwell method, whereas the expansion pressure, degree of swelling, and agglutinating number did not change appreciably. Samples selected from the middle of the stored lumps of these 4 coals behaved similarly. The suggestion was advanced that the decided increase of the softening point caused by storage was due to the secondary constituents in the bitumens, whose presence and melting points do not appreciably affect the other three properties.

Lambris concluded that the sensitiveness

of the four important coal properties—softening point, expansion pressure, degree of swelling, and caking—decreases in the order named. In other words, one of these properties can be destroyed within its conversion range by prolonged preheating in an inert atmosphere at low temperatures (200° C) or by storage in a limited amount of air without affecting materially, or at all, the next named property or properties in the series.

In a later study Lambris¹⁶⁹ investigated the effects of certain impurities, such as occur in commercial nitrogen, of the oxygen and sulfur (free and combined) in coke-oven gases and of the addition of boric acid upon the expansion pressure, softening behavior, and yield of distillation products of expanding coking coals. Preheating the bituminous coals in the presence of any of these agents at 100 to 200° C, even if their oxygen content was less than 1 percent, completely destroyed the swelling power of the coal; the tests using boric acid even gave a negative expansion pressure. However, boric acid mixed with coal and heated for 1 hour at 300° C in an oxygen-free atmosphere caused no change in the expansion pressure. The explanation given was that the boric acid was dissolved out again. On the contrary, when the coal was mixed with 0.3 to 0.5 percent of boric acid and heated progressively within the softening stage, the coal no longer showed expansion. The hypothesis was advanced that the boric acid formed complexes with the organic hydroxyl compounds, particularly with the phenols, and thus removed part of the normal cleavage products.

The expansion pressure (Damm method) of a coal giving a coke yield of 75 to 80 percent [Bochum method] was completely destroyed after heating with an admixture containing 0.5 percent boric acid. In

the Koppers apparatus a strongly expanding coal with the same amount of boric acid added gave similar results. With 1 percent addition of boric acid to the latter coal the tar yield was reduced from 5.0 to 3.5 percent, but with additions of 2 to 50 percent the tar yield remained constant at 3.25 percent. The yield of gases under the same conditions fell about a third, but the coke yield was increased about 2 percent. The tar produced from the coal directly was dark brown and viscous; that from the coal with the addition of boric acid was thinly fluid and yellow to yellowish brown, the yield of nonviscous oils was essentially greater, and those of phenols and benzene-insoluble were smaller. The evolved tar and gases were always found to be free of boric acid. The explanation was offered that a large part of the volatile products was fixed by the action of the boric acid. Tests of the cokes showed that 95 percent of the original boric acid remained in the coke; the other 5 percent was assumed to be volatilized with the water of decomposition.

Additions of boric acid to a bright-coal concentrate reduced the tar yield to 65 percent of that normally obtained from the bright coal. Similar treatments of splint-coal concentrates gave a 93 percent yield of the normal amount of tar from splint coal. The suggestion was offered that had the splint-coal concentrate been entirely pure no reduction in tar yield would have occurred.

The effect of the addition of increasing proportions of boric acid upon the softening curve of a fat coal (analysis not given) was studied. Softening curves were determined by means of a penetrometer method. Additions of 0.5, 1.0, 2.0, and 5.0 percent of boric acid did not affect appreciably the softening temperature of the coal but progressively reduced the depth to which the

needle sank into the coal briquet and changed the course of the softening curve up to the addition of 2.0 percent boric acid, above which further addition produced no changes.

Nedelmann⁹⁶ modified the test apparatus of Baum and Heuser.^{159, 61} Some additional information concerning the apparatus and test procedure, which was not apparent from the diagram of the apparatus or description in the original short article by Nedelmann, has been presented by Foxwell.¹⁶⁰ Foxwell gave both a photograph and an excellent diagram of the apparatus and described the test procedure in detail. He also suggested a set of tentative standards defining test conditions and the dangerous or safe expansion characteristics of coal. Nedelmann tested 3 coals, each containing 10 percent moisture. Expansion pressure values ranged from 0.19 to 0.40 kilogram per square centimeter, and duplicate tests checked within 0.01 to 0.02 kilogram per square centimeter. The percent shrinkage of 1 coal, tested at a charge density of 730 kilograms per cubic meter, checked exactly, whereas those of the other 2 coals, each tested at charge densities of 750 kilograms per cubic meter, both showed a difference of 0.6 percent in their duplicate tests.

Broche and Nedelmann⁶⁴ used the method of Nedelmann to measure the expansion pressure of bright and dull coals. Bright coals gave an expansion pressure of 0.42 to 0.65 kilogram per square centimeter, whereas dull coals showed no expansion pressure but gave a shrinkage of 7.8 to 10.5 percent.

Shimomura⁹⁵ also used the Nedelmann apparatus. The coal was charged with a moisture content of 10 percent and was compressed to a bulk density of 770 kilograms per cubic meter on the wet-coal basis. Shimomura divided caking coals

into two classes: "hard" and "soft." The "hard" coals were defined as those that showed an expansion pressure of about 0.1 kilogram per square centimeter. Results on Yubari and Hashima coals showed expansion pressures of 0.04 and 0.11 kilogram per square centimeter, respectively. When blended with 30 percent of (a) anthracite, (b) coking coal, (c) high-volatile, highly oxygenated coal, (d) oxidized coal, similar to (c), (e) 450° C semicoke, (f) 500° C semicoke, (g) coke breeze, and (h) quartz sand, no expansion pressure was observed in any of these blends. The (b) coking coal was stated to have an expansion pressure of 0.17 kilogram per square centimeter.

Schlöpfer and Müller⁸⁶ modified their swelling test apparatus (see page 197) to determine the expansion pressure of coals. Boltigen, Neümuhl, Heinitz, and La Houve coals showed expansion pressures of 0.42, 0.71, 0.38, and 0.17 kilogram per square centimeter and swellings of 81, 46, 25, and 2 millimeters, respectively. The lack of parallelism in the two sets of results was pointed out. The abnormal relationship of the results on Boltigen coal was explained by the fact that this coal formed a coke of fine, fused lamellae, which in the plastic state could not withstand a large counterpressure. Similar tests made upon these same coals, preheated at 250° C for 15 minutes, showed expansion pressures of 0.13, 0.16, and 0.13 kilogram per square centimeter, and swellings of 2, 0, and 0 millimeter, respectively, for the first 3 coals, and zero expansion (no coke formation) and only a powder for the La Houve coal. Preheating of the coals had caused an almost complete loss of their individual characteristics, explained by the loss of swelling capacity of the solid bitumens. The measured pressures seemed to be limited solely by the structure-loosening (pore-

widening) theory of Damm. Briefly, this theory postulated that the loosening of the structure of the coal produced by heating leads to a change in volume of the charge which actually is the cause of the expansion pressure.¹⁷³

Taylor¹⁷⁴ determined the "actual swelling pressure" exerted by the swelling of the plastic layer of coal, apart from the neutralizing effects of counterpressure produced by compression of the coal outside of the plastic layer and by secondary contraction of coke already formed. For this objective, he used a modified Damm-Hofmeister apparatus.

A large number of high-agglutinating-value coals were tested and the results correlated with the tendency of the coals to produce "spongy" coke under commercial conditions. Eight of the coals tested had previously been coked in an actual battery, and 7 of the coals in an 18-inch experimental oven. In each instance, the carbonizing time was 18 hours. Spongy cokes were produced in the battery from coals showing pressures in the test apparatus using loads above 45 to 50 kilograms, and in the experimental oven from coals showing pressures under loads of 50 to 55 kilograms. The lower limiting pressure in the battery was attributed to the greater height of the oven—14 feet, as compared with 8 feet in the experimental oven—with consequent increase in bulk density in the oven battery. Taylor did not convert his measured kilogram values, called "swelling pressures" by him, into the more commonly expressed kilograms per square centimeter pressure units. He believed that before this is done tests should be carried out in retorts of different cross sections.

Taylor defined two kinds of sponge: (a)

¹⁷³ Damm, P., *Brennstoff-Chem.*, **10**, 191-5, 217-21 (1929).

¹⁷⁴ Taylor, J., *Fuel*, **10**, 390-3 (1931).

attached sponge, which sometimes is found on the inner ends of coke, and (b) detached sponge, or the mass of sponge formed above the top of the charge. Some coals, even those with low swelling pressures, showed prominent attached sponge, which was assumed to be the result of secondary contraction as much as of swelling pressure. The theory was advanced that, near the end of coking in the coke oven, the final last inch or so of coal is carbonized as an open texture and spongy coke, or attached sponge.

The swelling pressure of a number of differently proportioned blends of two coals was determined. The experimental values checked fairly well those of values calculated on the assumption that the swelling pressure of a blend is the arithmetical mean of that of its constituent coals. Some tests also were made on the effect of the constituents of ternary blends in reducing swelling pressure.

A decrease in bulk density, brought about either by lower compression of the charge or by addition of water, lowered the swelling pressure. This swelling pressure increased with increase in rate of heating up to a certain maximum, and then decreased. The addition of 5 percent of shale passing a 90 I.M.M. sieve to a coal with a swelling pressure of 60 kilograms caused no material change. The addition of 20 percent of coke passing a 90 I.M.M. sieve to a coal of greater than 60 kilograms swelling pressure reduced this to 30 kilograms. An addition of 20 percent of coke between 30 to 60 I.M.M. sieve caused but little change, and even with a 25 percent addition the swelling pressure was still 40 kilograms. The results showed that a large amount of coke breeze was required to reduce the swelling pressure of a very highly swelling coal, and the efficiency of

the addition fell rapidly with increasing particle size.

Taylor pointed out that the highly swelling English coals that he tested and that showed detached sponge caused no damage to the oven walls. As compared with German coals, which were known to cause damage, he suggested that the English coals probably gave higher secondary contraction and that the dangerous peak pressure that occurred, according to Koppers, at 4 to 6 hours before the end of carbonization was partly released by the frothing, which led to sponge formation. Furthermore, all the English coals tested were high-agglutinating coals, as compared with the lower-agglutinating German coals.

Five of the coals tested by Taylor showed swelling pressures greater than 60 kilograms, which would amount to more than 7.1 kilograms per square centimeter on the 8.5 square centimeters cross section of the tested coal charges. No comparable values on the same English coals are available, but swelling pressures of more than 7.1 kilograms per square centimeter are undoubtedly higher than would be observed by the usual laboratory expansion pressure test methods, because they allow a part of the actual pressure developed to be neutralized by compression of the coal outside of the plastic layer and by secondary contraction of the coke already formed.

Hock and Fritz¹⁷⁵ held the volume of coal constant and measured the change in pressure. The effect of bulk density, ranging from 0.700 to 0.800 gram per cubic centimeter on the dry-coal basis, was determined to be virtually a straight-line function. An increase in bulk density of about 3 percent caused an increase in expansion pressure of approximately 0.0275

¹⁷⁵ Hock, H., and Fritz, E., *Glückauf*, 68, 1005-12 (1932).

kilogram per square centimeter (an average of about 7 percent).

Bright and dull portions separated by hand from 7 Ruhr coals showed the following analyses and agglutinating numbers:

COAL SEAM	ASH, percent		VOLATILE MATTER (PURE COAL), percent		MEURICE AGGLUTINATING NUMBER, kilograms	
	Bright	Dull	Bright	Dull	Bright	Dull
Dickebank	1.7	20.2	17.2	19.1	22.1	0.0
Hermann	0.5	11.4	18.0	13.0	23.5	0.0
Röttgersbank	1.5	8.0	19.5	17.5	25.1	0.0
Dickebank	0.6	17.4	21.3	19.7	22.7	0.0
Röttgersbank	3.0	24.3	22.2
Zollverein 3	0.7	4.6	22.0	45.0	15.6	10.4
Flöz H	0.3	0.8	29.1	37.6	15.2	5.0

Expansion pressures, expansion times, and shrinkages were determined on the 7 bright portions and on 9 blends of the first 4 of these with additions of 5, 10, 15, or 20 percent of the corresponding dull portions of the same coals. The expansion pressures of the 7 bright coals in kilograms per square centimeter and their agglutinating numbers, plotted as ordinates against their volatile-matter contents as abscissas, were found to express similar general relations. The expansion pressures, expansion times, and agglutinating numbers of the 4 bright coals and their 9 blends were plotted as ordinates against the decreasing amounts of bright coal as abscissas. The curves showed a fairly regular decrease in the ordinate values with decreasing amounts of bright coal. Fine grinding of the dull coal gave a greater reduction in the expansion pressure than was shown by similarly ground bright coal.

Davies and Mott⁸² determined the swelling pressure of 6 English coals by a modified Sheffield laboratory coking test. The pressure, in pounds per square inch, required to prevent the expansion of Silk-

stone coal was 300; of Parkgate, 600; of R. M. Barnsley, 750; and of Busty, Brockwell, and Two Foot Nine Seams 800 pounds per square inch each. The coals, in the order listed, contained approximately 86,

85, 84, 88, 89, and 89 percent of carbon on the dry, ash-free basis.

Bleibtreu and Jung¹⁴⁸ used the Hofmeister method⁶² to determine the expansion pressures of Bahnschacht and Tiefbau coking coals and of their 80:20 blend. Bahnschacht coal showed a maximum expansion pressure of 0.41 kilogram per square centimeter after 30 minutes' heating and then began to shrink almost immediately. Final shrinkage amounted to 5.5 percent. This coal when coked in a small-chamber oven 1,000 centimeters long, 200 centimeters high, and 35 centimeters in average width produced a coke of 73 to 78 drum strength. Tiefbau coal gave a maximum expansion pressure of 0.30 kilogram per square centimeter after about 40 minutes of heating, which dropped only to about 0.24 kilogram per square centimeter after 80 minutes of heating, but then dropped more rapidly. A final shrinkage of 6.0 percent was observed. A weak, fissured, splintery coke was produced in the small-chamber oven. After 50 minutes' heating, the blend coal showed a maximum expansion pressure of 0.50 kilo-

gram per square centimeter, which then dropped rapidly. Final shrinkage of 5.5 percent resulted. The coke produced from this coal in the small-chamber oven was of about the same strength as that from the Bahnschacht coal.

Bunte and Imhof¹³⁶ devised an apparatus that was somewhat similar in principle to that of the constant-volume apparatus of Damm but was designed expressly to enable both the expansion pressure (*Treibdruck*) and swelling (*Blähen*) of a thin layer of coal to be determined in individual temperature zones and was adapted particularly to the testing of borderline coals.

The surprising result of the investigation was that all caking coals, whether they were known as suspiciously expanding or as harmless, gave expansion pressures amounting from 1.5 to 5.0 kilograms on the total surface, or up to a maximum of 0.5 kilogram per square centimeter, in the temperature range from below 100 up to near 400° C. The maximum expansion pressure values were given around 320 to 350° C. This pressure effect then disappeared almost completely, but, at the Foxwell fusion temperature of the coal sample, a second, weaker pressure developed, which, after a temperature rise of about 20° C, again disappeared when the coal became fluid enough. The authors stated that this second rise in pressure obviously corresponded to that which many other workers have designated as expansion, namely, a pressure that develops as a result of the lack of immediate escape of gases suddenly generated in the fused coal, thus giving the effect of swelling. In some coals a third pressure set in, also due to swelling, at the temperature of resolidification of the fused coal mass. In nonfusing coals no pressure developed below 400° C; only the small pressure due to the imper-

fect escape of gases appeared above 400° C.

The swelling curves were determined with the same apparatus with the piston unloaded and free to move. Swelling did not occur until near 400° C, and it became pronounced in the fusion range of the coal. In addition to expansion pressure and swelling, the proximate analyses, Foxwell softening curves, and gravimetric degasification curves also were determined. Tests were made on 14 German coals grouped as follows: 1 noncaking, sintering coal from Upper Silesia; 2 Saar and 2 Ruhr nonexpanding caking coals; 7 expanding caking coals, 3 from the Wurm, and 1 each from the Ruhr, Upper Silesia, Ungarn, and Aachen districts; and 1 Saar and 1 Ruhr coal intermediate in properties between the first two groups.

Swelling was attributed to the portion of the coal extractible by pyridine, chloroform, or benzene. To support this hypothesis the Upper Silesian expanding caking coal (27.8 percent volatile matter, pure-coal basis) was subjected to a number of special tests. After this coal had stood for 10 days in pyridine vapor its maximum expansion pressure was reduced from 4.2 kilograms, or 0.42 kilogram per square centimeter, to almost zero, and the swelling at 440° C was reduced from a maximum of around 22 to 13.5 millimeters.

Addition of 15 percent of coke powder to this same coal reduced the expansion pressure to 1.5 kilograms and the swelling to 20 millimeters. Addition of 1 percent of boric acid increased the expansion pressure to 5.6 kilograms and the swelling to 39 millimeters. This effect was contrary to the observation of Lambris,¹⁶⁹ who found that strongly expanding fat coals (analyses not given) completely lost their property of expanding pressure when treated with only 0.5 percent of boric acid. Lambris observed the same effect in tests by both the

Korten-Damm constant-volume and the Koppers A.-G. constant-pressure types of apparatus. The differences in results obtained by the two investigators have a possible explanation in the difference in the ranks of the coals tested. Bunte and Imhof used a coal that gave a pure coke yield of 72.8 percent, whereas the coals used by Lambris gave coke yields between 75 and 80 percent. The layer of coal heated by Bunte and Imhof was also much thinner than that heated by Lambris. The coal tested by Bunte and Imhof was stated by them to be fairly fluid and gave a strong increase in swelling. Lambris found, also, that if coal was heated in the presence of boric acid for 1 hour at 300° C the expansion pressure was not affected as it was in the tests using progressive heating.

Preheating to 390° C of the Upper Silesian expanding caking coal in nitrogen reduced the expansion pressure to 3.2 kilograms but produced no effect on swelling. The same treatment at 460° C reduced the expansion pressure to 2.5 kilograms and almost completely destroyed the swelling. On heating in a stream of air for 4 hours at 150° C the expansion pressure was reduced to 1.3 kilograms and the swelling to 20 millimeters, whereas with the same treatment at 250° C the expansion pressure was reduced to 1.0 kilogram and the swelling to 9 millimeters.

Shimomura⁵ preferred the term "driving pressure" to the more common "swelling pressure." The driving pressure was determined by the Nedelmann test method⁹⁶ on 20 British coals and blends, including 3 from South Wales, 4 from Derbyshire, 2 from Yorkshire, 5 from Durham, 1 from Staffordshire, and 5 from Nottinghamshire. The "driving pressures" of the 20 samples ranged from zero to 0.40 kilogram per square centimeter and did not show the same order as the decreasing volatile-mat-

ter contents, from 20.5 to 37.9 percent. Shimomura set up criteria for a coal suitable for coke manufacture based on certain limits of the proximate, ultimate, and phenol extraction analyses, on data obtained by his K-B-S test methods (Type A, no load, and Type B, 74.5 grams per square centimeter load on the coal charge), on "driving pressures" obtained by use of Nedelmann's apparatus, and on the temperature range of maximum rate of evolution of volatile matter determined gravimetrically in his own apparatus. Numerical data on the 20 coals and blends were complete only for ash, volatile matter, fixed carbon, and driving pressures. Only the 3 South Wales and 4 of the Durham coals met the requirement (20 to 30 percent, dry basis) for volatile matter. Of these 7 coals, 3 of the Durham coals exceeded the maximum driving pressure allowable, namely, 0.1 kilogram per square centimeter.

Mott and Spooner^{161, 165} used the constant-volume types of test methods developed by Baum and Heuser^{159, 61} and by Nedelmann⁹⁶ in a comparative study of expansion pressures determined by seven different test methods. A summary of the results obtained will be given later.

Larger-Scale Swelling Test Apparatus or Small Experimental Test Ovens. Test-oven methods for determining the expansion pressure of coal differ primarily from the smaller-scale laboratory crucible test methods in the size of the coal charge used. Charges of 4 to several hundred pounds of coal are carbonized under conditions approaching more nearly those occurring in a commercial coke oven. Some of the test ovens also depart from the usual older design; instead of a cylindrical charge, the test chamber is constructed to receive a charge shaped like a rectangular parallelepiped. Unidirectional heating is carried out either from the bottom or from one

side of the charge or, more recently, from both sides of the charge.

H. Koppers^{180, 181, 176} designed a "large-scale swelling apparatus" in which the behavior of coals at various bulk densities was examined. The earliest date of development or the date of the cited description was not stated. The apparatus differed from the earlier laboratory apparatus¹⁵⁸ chiefly in size. Only pressures generated in the coal charge greater than 0.08 kilogram per square centimeter—the pressure which Koppers and Jenkner⁵⁹ regarded as the "permissible" load on a coke-oven wall—were measured.

The "crucible" had a perforated bottom and when charged was set in a suitable gas-fired or electric furnace, the annular space between being filled with loosely packed coal. Heat was applied only to the bottom of the charged crucible, so that any expansion of the coal took place, as in a coke oven, in the direction of the flow of heat. The rate of heating was adjusted to complete the carbonization in 16 to 20 hours, as in plant operation.

If the swelling pressure exerted by the coal during the test exceeded 0.08 kilogram per square centimeter, the plunger and the lever were raised. After 8 to 10 hours of heating, any expansion above the "zero" or 0.08 kilogram per square centimeter datum line was completed. The shrinkage of the charge was then determined. If the coal charge showed a pressure greater than 0.08 kilogram per square centimeter, it was considered *unsafe* for coke-oven use. Every good coking coal will develop a dangerous swelling pressure if the bulk density of the charge is increased enough. For this reason Koppers recommended that each coal or blend be tested at several bulk densities, covering the range that might be obtained

in charging commercial coke ovens. Test curves obtained at bulk densities of 750, 800, 850, and 900 kilograms per cubic meter (dry basis) showed that dangerous swelling pressures were developed with two different coals at bulk densities above 800 kilograms per cubic meter. The information proved useful in investigating coals from different mines and seams and in making a proper selection of such coals for coking alone or for blending without resultant harm to the coke oven.

The usefulness of this type of test for determining the expansion pressures of a given coal charge in different positions in the coke oven and at various bulk densities caused by different heights of drop during charging was suggested. Coal charges consist of coal, air, and moisture. The farther the charge drops during charging, the smaller the spaces between the individual coal particles become because of the escape of part of the air. It follows, therefore, that the coal on the oven sole under the charging holes has a greater bulk density than the average of the charge. This is augmented by the fall of the fine coal toward the bottom of high ovens.

To establish the bulk density of the coal charge at different points in a coke oven, Bunte and Imhof¹³⁶ have suggested that a separate concrete oven chamber should be built at the end of each coke battery, exactly similar in dimensions to the other ovens. The chamber should be arranged so that the coal can be charged and leveled just as in any of the ovens proper. The side wall of the chamber should be provided with numerous suitably placed openings for the extraction of coal samples at various levels under and between the charging holes, by means of which a given volume of coal can be cut out of the charge and its bulk density determined. The highest bulk density determined in this way

¹⁷⁶ Koppers, H., Publication of H. Koppers G.m.b.H., Essen, Germany, 1937, 12 pp.

may be used as the basis for the expansion pressure tests of the coal in the swelling test apparatus. According to Foxwell¹⁶⁰ the Beckton plant of the Gas Light & Coke Company in England, where Durham coals generally are carbonized, has such a concrete test chamber.

Altieri¹⁷⁷ outlined briefly the results obtained by the Massachusetts gas companies between 1905 and 1935 with various types of tests that enabled conclusions to be drawn upon the critical factors that should be considered in the design of a coal expansion test apparatus. Out of the experience a unidirectional heating apparatus, known as the Type A coal expansion tester, was developed. This tester was designed: (1) to impart a unidirectional flow of heat into the coking charge; (2) to produce a plastic zone analogous to that which occurs in a section of a plant oven; (3) to produce temperature and material gradients in a plane perpendicular to the plane of the plastic zone that are more or less similar to those that occur from the coke-oven walls to a parallel perpendicular plane at the center of the oven; and (4) to permit external movement of the piston only in a direction perpendicular to the plane of the plastic zone, thereby simulating the side thrust against the oven walls.

Data obtained in the Type A tester on high-volatile and low-volatile coals and on blends of these coals indicated that the maximum difference between duplicate tests on the same sample was too great in borderline coals. Supplementary studies on the nature, shape, and rate of movement of the plastic zone of the coal charge during coking suggested that the design of the tester should be changed to prevent conduction of heat by the piston rod into the

surrounding coal charge, thereby distorting the plastic zone. Furthermore, to reduce side coking to a minimum and to produce a reasonably flat plastic zone, other desirable changes in apparatus and test procedure were indicated. Out of these experiences was developed the Type B tester.

In the B tester, expanding coals showed a consistent contraction for the first hour or two and then expansion up to a maximum just before the end of coking. Altieri suggested that this initial slump may be due, in part, to general internal changes that precede the attainment of initial equilibrium, that is, to the sudden change in coefficient of internal friction of the coal charge that resulted from initial evolution of moisture and gas that diffused through the coal charge just before the plastic zone was formed; or the slump may be due to the formation of the plastic zone itself. Altieri recognized the effects of thermal expansion of the test apparatus and its influence on the observed expansion under different conditions for different coals. To avoid the error introduced in the usual nomenclature for expressing expansion, he proposed the term "apparent linear expansion," which "measures pressure or expansion perpendicular to the plastic zone and neglects relatively small linear changes in a direction parallel to the plastic zone." This distinction is a good one because it is in keeping with experimentally observed data. The elastic characteristics of the apparatus as well as the thermal expansion during the progress of coking must be known and a suitable correction must be made for them to get true linear expansion.

Altieri's Type A and Type B testers have received favorable attention and have been used in a number of laboratories in the United States and Canada. Brown¹⁷⁸ re-

¹⁷⁷ Altieri, V. J., *Gas Age-Record*, **76**, 49-54 (1935); *Proc. Am. Gas Assoc.*, **1935**, 812-36; *Am. Gas J.*, **143**, No. 5, 43 (1935).

¹⁷⁸ Brown, W. T., *Proc. Am. Gas Assoc.*, **1938** 640-79.

ported some unpublished data by the Canadian Bureau of Mines on Michel (Canadian) coal determined by both the Altieri Type A and Type B testers. Unreliable check results by the Type A tester were explained as due to variations in loading the charge and to varying quantities of sponge coke or uncoked coal found in the residue after the test.

Altieri¹⁷⁹ has given a brief description of the Type C tester which measures simultaneously the change in depth and the change in width of a coal during its coking. The width of the charge could be varied up to about 8 inches by setting a cold rectangular side wall. The side wall was connected to a device that imposed a side thrust up to about 6 pounds per square inch. Provision was made also to apply any desired downward pressure. With the Type C apparatus it was possible to concentrate study upon five factors: horizontal and vertical load, horizontal and vertical expansion or contraction, and compressibility of the coal charge during coking.

Three tests were carried out in this tester on a high-volatile coal at vertical loads of $\frac{1}{2}$, 1, and 2 pounds per square inch, respectively, and each kept under a horizontal load of about 2 pounds per square inch. The first test gave a horizontal contraction of 11.7 percent and a vertical expansion of 2.9 percent. In the second test these values were 10.8 and 1.3 percent, respectively. The third test showed a horizontal contraction of 5.8 percent and a vertical contraction of 1.4 percent. Altieri stated that the overall volume shrinkage due to coking in the first test was 8.9 percent and in the third, 7.1 percent, "although one would expect that the greater vertical

load would cause a greater overall shrinkage. The vertical load is partly translated into horizontal reaction. Hence, although the horizontal load is about the same, the horizontal contraction changes from about 12 to about 6 percent.

Altieri found that definite coal expansion properties may be determined in a definite relationship between stress and strain. Some of the tests in the Type B tester were carried out under conditions such that the tendency of the coal charge to expand was restrained by different amounts as a result of varying the amount of the load used. The *stress* imposed by the piston on the coal charge in pounds per square inch perpendicular to the plastic zone was plotted against the *strain* or fractional change in the width of the coal carbonized. The individual ordinates represented the stress in pounds per square inch on the successive charges of the coal; the abscissas showed the observed maximum lateral expansion, or strain. The maximum side thrust was indicated at the intersection of the stress-strain curve and the line of zero strain. Expansion or strain, here, was not produced by the corresponding stress, as in testing-materials practice. Both stress and strain were produced by a third condition, namely, the coking process. One may assume that the coke produced was perfectly elastic. Then, to restore the original dimensions, it would be necessary to compress an expanded charge and to release the pressure on a contracted charge. Hence, the maximum stress due to coking an expanding coal was found on the diagram at the point of zero strain, and the curve sloped downward to the right.

When coked in a model oven simulating coke-oven practice, a coal blend, a medium-volatile coal, and a low-volatile coal showed expansion pressures, or maximum stresses, of 0.8, 2.3, and 5.8 pounds per square inch,

¹⁷⁹ Altieri, V. J., Paper presented at Joint Comm. Conf. of Production and Chemical Comm., Tech. Sec., Am. Gas Assoc., May 23-25, 1938, New York, N. Y., 8 pp. (mimeographed).

respectively. By using the maximum positive strain for different stresses plotted in the diagram, the values indicated for the modulus of elasticity, namely, the ratio of the increment of unit stress to unit deformation within the elastic limit, were maximum values. When the modulus was very large it showed that the charge will exert a relatively greater force if it is restrained so that a small deformation cannot take place. If different expanding coals show about the same maximum side thrust one would prefer to carbonize those that show low values for modulus of elasticity because they would exert forces that change at low rates and therefore would cause less fatigue of the oven walls. The value of the modulus that is of importance in selecting coals for carbonization would correspond with the values obtained with safe coals and would be a measure of the working stress.

Brown^{178, 180} modified the Altieri Type B tester in several respects and used it for 325 expansion tests. All were run at a flue temperature of 2,350° F measured directly under the floor of the tester; the applied pressure was 2.2 pounds per square inch on the coal charge, and the coking time was 18 hours. Duplicate tests checked within 0.1 to 0.2 inch per foot depth of coal charged. The tester appeared to be satisfactory for measuring the expansion of low- and medium-volatile coals but was unsatisfactory for determining the contraction of high-volatile coals. Some side-wall coking was observed, showing that the heating was not entirely unidirectional from the bottom of the test pot. The long time of coking, 18 hours, was objectionable for test economy. Forty-seven different coals from the Pocahontas district were tested.

Twenty-five of these coals were from the

Pocahontas No. 3 Seam. Their volatile-matter content (dry, ash-free basis) ranged from 16.5 to 24.5 percent. The coals included: 13 from McDowell County, 4 from Mercer County, 3 from Raleigh County, 2 from Wyoming County, and 1 from Fayette County, W. Va.; and 2 from Tazewell County, Va. Expansion curves for these 25 coals, with expansion in inches per foot of coal plotted against coking time in hours, showed a range from 0.1 inch contraction to 2.7 inches expansion per foot of coal. Similar tests were carried out on 5 Pocahontas No. 4 Seam coals, all from McDowell County, W. Va.; 2 Pocahontas No. 5 Seam coals, 1 from McDowell County, W. Va., and 1 from Tazewell County, Va.; 7 Beckley Seam coals, 6 from Raleigh County, W. Va., and 1 from McDowell County, W. Va.; 5 Sewell Seam coals from Raleigh County, W. Va.; and 1 coal each from the Eagle Seam, Logan County, Dorothy Seam, Kanawha County, and Fire Creek Seam, Fayette County, W. Va.

Wide variations in the expansion pressure curves were found, both for different coals from the same seam and for coals from different seams but from the same county. Two Pocahontas No. 3 Seam coals from Tazewell County, Va., 1 from McDowell County, W. Va., and 2 Pocahontas No. 5 Seam coals, 1 each from these same two counties, showed final coke volumes less than their original coal volumes. The other 42 coals were still expanded at the end of the 18-hour coking time.

The results of the expansion tests on these 47 different coals from the Pocahontas district were plotted by using percent expansion as ordinates against percent volatile matter on the dry, ash-free basis as abscissas. Smooth curves were obtained for coals of like ash contents. For coals of a given volatile-matter content, the expansion pressure was larger for the coal

¹⁸⁰ Brown, W. T., *Blast Furnace and Steel Plant*, 27, 172-4 (1939).

having the least ash. These curves were reported to be of great value in purchasing coals and making suitable blends of them to avoid damage in the coke ovens.

Brown^{178, 180} also designed and developed the "Bethlehem tester," a miniature sole-flue coke oven, 11 inches wide by 36 inches long. It was heated unidirectionally by gas. The flue temperature directly under the tester floor was held at 2,350° F. The pressure on the coal sample was maintained at 2.25 pounds per square inch, and the coking time was 8 hours.

Brown in a private communication has stated that he used as division limits between anthracite and semianthracite, semi-anthracite and low-volatile bituminous, low-volatile bituminous and medium-volatile bituminous, and medium-volatile and high-volatile bituminous coals the corresponding percentages of 14.3, 16.5, 23.0, and 31.0 volatile matter on the dry, ash-free basis.

The percent expansion of 33 low-volatile Pocahontas coals was determined in the Bethlehem tester. The data obtained indicated that the expansion ranged from 2.4 to 20.7 percent with decrease in volatile-matter percentage from 24.5 to 16.5.

Thirty-one different high-volatile coals from the Pittsburgh Seam showed contractions ranging from 7.8 to 27.2 percent. This wide range shows the importance of determining the contraction of all high-volatile coals.

Four samples from the Upper Freeport Seam, ranging in volatile-matter content from 33.28 to 18.62 percent, ranged in expanding properties from a contraction of 15.6 percent to an expansion of 23.7 percent. Four medium-volatile coals from the Lower Freeport Seam, from Indiana County, Pa., showed rapid expansions followed by marked contractions. The most-expanding coal contained 29.9 percent volatile matter and expanded rapidly for the

first 4.5 hours up to 12.5 percent and then shrank to 8 percent expansion at the end of the 8-hour coking test period. The least-expanding coal contained 32.0 percent of volatile matter and expanded during the first 4 hours up to 5.0 percent and then shrank to 0.4 percent expansion at the end of 8 hours. The other two Lower Freeport Seam coals showed intermediate expansion, around 11.0 and 11.4 percent, and shrinkages to about 6.4 percent expansion.

Five Upper Kittanning Seam coals, all from Johnstown, Pa., and vicinity, showed a decrease in expansion with increase in volatile-matter content. Similar straight-line relationships, but with different slopes, were found for other low-volatile coals from the Pocahontas and Lower Kittanning Seams.

The effect of geology of the coal seam on expansion was determined on 5 channel samples, a run-of-mine sample, and a washed sample of the last, all from the Upper Kittanning Seam of the Franklin mine, near Johnstown, Pa. Their volatile-matter content ranged from 19.4 to 23.4 percent, and their expansion from 2.2 to 19.3 percent in a somewhat linear relationship. The increased expansion of the washed sample above that of the run-of-mine was attributed to its lower ash content. Six channel samples of coal from different sections of a mine in the Lower Kittanning Seam, also near Johnstown, Pa., did not show such wide variations.

A study of expansion in relation to progressive coalification was made on samples from 56 different mines in the Lower Kittanning Seam in Pennsylvania and West Virginia. Percentages of maximum expansion or contraction, plotted as ordinates against volatile-matter percentages as abscissas, showed that the coals could be divided according to rank from the shape of certain segments of the curve. The per-

centage of expansion decreased rapidly from a maximum of 45.8 to approximately zero for the low-volatile coals (16.5 to 23.0 percent volatile matter, dry, ash-free basis); then rose to 16.5 percent expansion and dropped again to zero for the medium-volatile coals (23 to 31 percent volatile matter, dry, ash-free basis); and finally fell from zero to 32.5 percent contraction for the high-volatile coals (over 31 percent volatile matter, dry, ash-free basis). Also, the relation between the hydrogen content of the coal and its expansion followed closely that shown between volatile-matter content and expansion. This was substantiated by an almost straight-line relationship between volatile-matter and hydrogen content. The carbon content and expansion also followed the volatile-matter and expansion curve. No relationships were found between oxygen content and percentage of expansion, the H/O ratio and expansion, or oxygen and volatile matter.

Curves showing expansion tests of low-volatile Pocahontas, Upper Kittanning, and Lower Kittanning Seam coals indicated that the expansion for samples of a given volatile-matter content increased in the order named. No tests were made on medium- or high-volatile coals from the Pocahontas and Upper Kittanning Seams, but one test on medium-volatile coal from the Sewell Seam indicated that other medium-volatile coals would show expansion similar to those from the Lower Kittanning Seam.

Four anthracites and semianthracites seemed to contract in proportion to their volatile-matter content. Of interest here is the fact that a semianthracite with 14.3 percent volatile matter (dry, ash-free basis) contracted and did not coke, yet a low-volatile bituminous Lower Kittanning Seam coal with 16.5 percent volatile matter (dry, ash-free basis) expanded 45 percent and yielded a hard, dense coke.

A series of tests on low-volatile and another on high-volatile coal were made to determine the effects of varying the applied pressure on the expansion and of no added load on the piston on the "free swelling" of the coal charge. With no added weight on the piston, a low-volatile expanding Lower Kittanning Seam coal showed a free swelling of 82.5 percent and produced a coke that was light and porous but of good appearance. With increasing applied pressures, the corresponding expansions decreased. Similar tests on a high-volatile, contracting coal from the Pittsburgh Seam showed a free swelling of 43.3 percent but produced a coke of poor quality and appearance and of very porous and honey-combed structure. Under a pressure of 1.0 pound per square inch, contraction of about 17.5 percent resulted; and under a pressure of 2.3 pounds per square inch, the contraction was about 26.4 percent.

The ash content of an Upper Kittanning Seam coal was reduced in successive steps by float-and-sink. The tests indicated that the purer the coal the greater was the resulting expansion for a coal of given volatile-matter content.

Addition of fusain synthetically to an Upper Freeport Seam coal already containing 3.9 percent of fusain to increase this to 12.7 percent lowered the expansion from 5.5 to about 1.2 percent and the shrinkage from 3 percent expansion to 1 percent contraction. The original coal gave its maximum expansion after 4 hours of coking time, whereas that with added fusain occurred at 3 hours of coking time.

At flue temperatures of 1,700 and 1,900° F, 12 hours was required to coke a low-volatile, expanding Lower Kittanning Seam coal; at 2,000° F, 10 hours; and at 2,150 and 2,350° F, only 8 hours. The rate of expansion was slower for the lower temperatures, and at 1,700° F the maximum

expansion was much less than the nearly equal expansion of 33 to 35 percent for all temperatures above 1,900° F. The results illustrate that a coal or coal blend may be expanding at fast coking time but safe or nonexpanding at lower temperatures or slower coking times.

A series of tests on samples of the same coal containing 0.0, 2.5, 5.0, 7.5, and 10.0 percent moisture indicated that, except for the dry coal sample, which expanded less than the sample containing 2.5 percent moisture, the percentage of expansion decreased with increase in moisture content. The tests were not considered conclusive, because bulk density and possibly other factors entered in, and only one coal was tested.

Tests on a fresh, highly expanding, air-cleaned slack coal from the Lower Kittanning Seam were made each month for 15 months. The original fresh coal contained 3.14 percent oxygen and showed an expansion of 43.0 percent; after 15 months of weathering it contained 5.35 percent oxygen and showed only 11.8 percent expansion. The coke from the freshly mined coal was hard, dense, and of good quality; that from the coal after 15 months of weathering was very granular and friable, was of very poor quality, and contained a large amount of fine coke. A series of tests on a highly expanding, low-volatile coal that had been in storage for 3 to 6 months and was badly oxidized also showed a very considerable reduction in expansion and produced considerable loose, sandlike coke.

Reducing the proportion of low-volatile Lower Kittanning Seam coal from 40 to 38 percent in blends with high-volatile Pittsburgh Seam coal rendered the second blend safe for coking, whereas the first blend was dangerous and even caused "stickers." The blend containing 40 percent Lower Kittanning Seam coal showed expansion up to 3.9

percent after 3.5 hours and shrinkage to about 1 percent expansion at the end of 8 hours. The blend containing 38 percent of this coal at the corresponding times gave an expansion of only 1.3 percent and a final shrinkage to about 1.1 percent contraction.

A ternary blend of 20 percent low-volatile Lower Kittanning Seam, 40 percent medium-volatile Lower Freeport Seam, and 40 percent high-volatile Pittsburgh Seam coals showed an expansion of 5.5 percent at the end of 4 hours and a shrinkage to 1.0 percent expansion at the end of 8 hours. When these proportions were changed, respectively, to 22, 20, and 38 percent, the blend was definitely contracting; 1.2 percent contraction at 0.5 to 1.75 hours after the start of the coking period, rising to 0.5 percent contraction at 3 to 3.5 hours, and then dropping to a constant volume of 4.1 percent contraction after 6.5 hours.

Constant-Volume Modification of the Bethlehem Tester. The Bethlehem tester was modified by inserting bricks exactly 4 inches in thickness at each end of the carbonizing chamber to support the piston, thus assuring a constant volume of charge no matter what the bulk density or pressure. Standard test conditions included a bulk density of 52 pounds per cubic foot, a pressure of only 1.5 pounds per square inch, and a moisture content in the charge of not over 2 percent. The constant-volume tester should be used only for borderline coals or coal mixtures.

The relationship between bulk density and expansion was determined. If the same bulk density was maintained, the size of coal did not seem to affect the results of expansion in the constant-volume tests.

The relationship between percent expansion and pressure in pounds per square inch for coals of 48, 50, and 52 pounds per cubic foot bulk densities was determined. Curves for each of these bulk densities were drawn

from a mathematical formula based on results at 1.5, 2.25, 2.5, and 3.0 pounds per square inch pressure. The three curves were extrapolated for pressures beyond these limits to cover a total range of pressure from 1 up to 5 pounds per square inch. The expansion dropped from above 8 percent at 1 pound per square inch pressure to about 0.7 percent at 5 pounds per square inch pressure for coals of 52 pounds per cubic foot bulk density, from 6 to about 0.5 percent for coals of 50 pounds per cubic foot bulk density, and from 1.8 to about 0.2 percent for coals of 48 pounds per cubic foot bulk density.

The effect of variation in temperature or coking time on the expansion of borderline coals of various bulk densities and at different pressures was determined. Tests at flue temperature of 2,350° F and coke temperature of 1,750° F were run for 8 hours. At bulk densities of 50, 52, and 54 pounds per cubic foot and a pressure of 1.5 pounds per square inch, the expansions were 2.1, 2.7, and 4.0 percent, respectively. With a bulk density of 50 pounds per cubic foot and a pressure of 2.25 pounds per square inch, the expansion was 2.0 percent. A second series of tests at 2,000° F flue temperature and 1,600° F coke temperature was run for 12 hours. At bulk densities of 50, 52, and 54 pounds per cubic foot and a pressure of 1.5 pounds per square inch, the expansions were 1.4, 2.0, and 3.3 percent, respectively. With a bulk density of 50 pounds per cubic foot and a pressure of 2.25 pounds per square inch, the expansion was 0.8 percent. The increased bulk density of the charge, when tested at the same pressure, caused expansion to increase. At the same bulk density but with increased pressure the expansion was reduced.

The U. S. Bureau of Mines¹⁸¹ developed

¹⁸¹ (a) Auvil, H. S., and Davis, J. D., *U. S. Bur. Mines, Repts. Investigations* 3403 (1938),

a sole-heated oven based upon the design of the Bethlehem tester. The Bureau found that, for comparison of expansion or contraction data obtained on different coals, it was highly desirable to make comparison at some chosen standard charge density, W_s . A standard charge density of 54.3 pounds per cubic foot, $W_{54.3}$, was chosen. It is inconvenient and sometimes impossible to adjust experimentally the test charges of different coals to a desired standard charge density. However, by selecting a unit volume of coal, 1 cubic foot, as a basis, the fractional expansion or contraction E_t , experimentally observed in a charge with an experimentally determined charge density W_t , may be calculated, from the weight of *solid* coal, W_c , in the charge, to the fractional expansion, $E_{54.3}$, at the standard charge density, $W_{54.3}$. Thus,

$$E_{54.3} = \frac{\frac{W_c}{W_t}(1 + E_t) - \frac{W_c}{W_{54.3}}}{\frac{W_c}{W_{54.3}}}$$

W_c may be computed from the true specific gravity of the coal tested. However, the equation may be simplified to read

$$E_{54.3} = \frac{W_{54.3}}{W_t}(1 + E_t) - 1$$

so that W_c need not be determined. Any other desired standard charge density, W_s , may be used for $W_{54.3}$. The validity of the equation for calculating the fractional expansion or contraction observed at any given experimental charge density to other selected charge densities has been demonstrated by the fact that the values thus calculated fall on a straight line of nearly the same slope as the straight line repre-

18 pp.; *Fuel*, 17, 335-48 (1938). (b) Auvil, H. S., Davis, J. D., and McCartney, J. T., *U. S. Bur. Mines, Repts. Investigations* 3451 (1939), 21 pp.

senting experimentally the fractional expansion or contraction values obtained at the same selected charge densities.

Two or more tests were made on each of 10 coals, ranging from strongly expanding to strongly contracting (volatile matter,

new standard density of 55.5 pounds per cubic foot. The greatest deviation of any test from its mean was only 0.5 percent. This was obtained on the coal containing 40.3 percent dry, mineral-matter-free volatile matter, although this coal did not

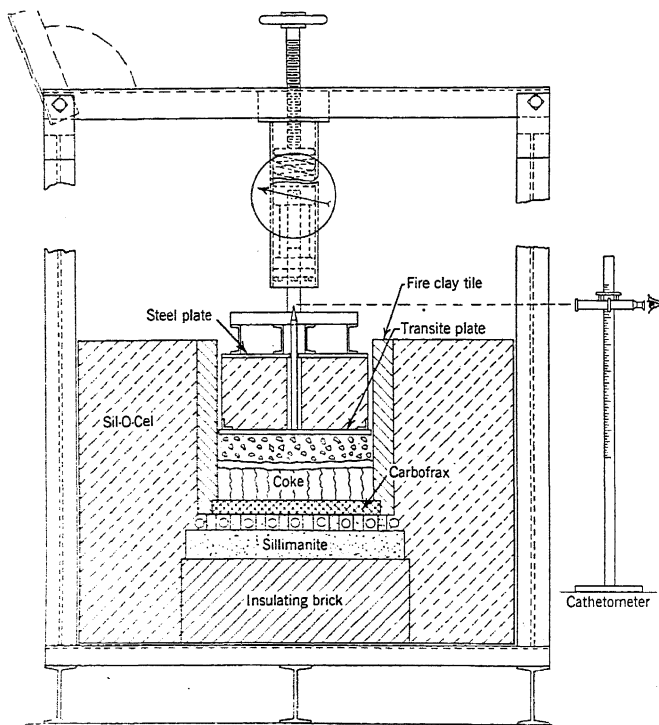


FIG. 9. Sole-heated oven for measuring expansion.¹⁸¹⁵

dry, mineral-matter-free basis, from 17.8 to 39.3 percent). The percent expansion or contraction found for the density of the charge used in each test was calculated to the standard density. The widest deviation of any test from its mean value was 1.7 percent, which was obtained on a strongly expanding coal containing 10.6 percent ash. Similar data were obtained on 14 coals (volatile matter, dry, mineral-matter-free basis, from 17.2 to 40.3 percent). These data were calculated to a

shrink as much as some others of slightly higher rank. In general, the lower the rank of the bituminous coal the greater the shrinkage or contraction. Conversely, the higher-ranking coals show high expansion. Depending upon the standard charge density taken as a basis or reference, coals with about 27 to 28 percent volatile matter (dry, mineral-matter-free basis) form the dividing point between contracting and expanding coals, according to data then available from the sole-heated oven.

Construction of the sole-heated test oven was changed to prevent deflection of the floor when constant-volume tests of the coal charge were made. The oven incorporating these changes is shown in Fig. 9. Tests at constant volume using a charge of Beckley Seam coal at 50 pounds per square

Fig. 10, used a 200-pound charge of coal in a vertical, steel retort. Results on 7 coals^{181a} showed that certain coals tended to give greater expansion in the slot-heated oven than in the sole-heated oven. This was found to be due to the greater density of charge near the bottom of the slot-

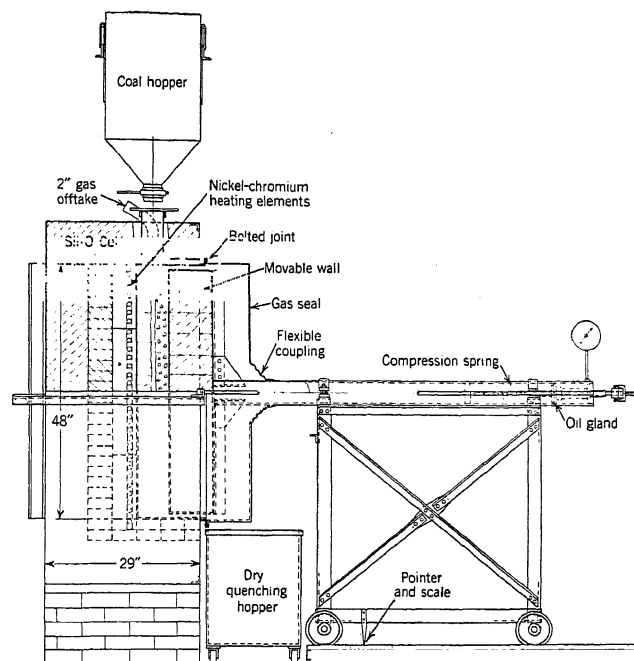


Fig. 10. Vertical-slot oven for measuring expansion.¹⁸¹

inch charge density showed that the pressure rose rapidly to 4.7 pounds per square inch, a total of over 1,000 pounds for the charge, which was the limit of the gage. The charge was then allowed to expand under a charge of 4.1 pounds per square inch. Expansion under this load at the end of the test was 1.4 percent. Tests indicated that it was impractical to work with coals of this type under constant-volume conditions.

The vertical-slot test oven developed by the U. S. Bureau of Mines,¹⁸¹ illustrated in

heated oven as a result of dropping the charge from the top of the retort. By allowing the movable wall to tilt at the center, the maximum expansion of Upper Kittanning Seam (washed) coal was reduced from 26.1 to 21.7 percent. Further work showed that this relation held generally for coals that developed little fluidity. High-volatile A coals are relatively more fluid, and apparently variations in bulk density from top to bottom of the charge are adjusted, regardless of whether or not the wall is allowed to tilt.^{181b}

Temperatures taken in the charge indicated that the plastic layer in the slot oven is about 10 percent thicker than that in the sole-heated oven. This would indicate that either the preheated wall or the longer path of the evolved gases in the slot oven affected the results. A pressure plate was made for the sole-heated oven similar in construction to that of the movable wall of the slot oven. This was preheated in the same manner as the wall of the slot oven during the warming and pretesting period. Results with the preheated plate were higher than those without and agreed more nearly with the expansions obtained with the slot oven. Just why this agreement should be found and why the use of the preheated plate in the sole-heated oven is unnecessary in tests with high-volatile coals to obtain checks by the two methods has not been established.

In comparing results obtained with the sole-heated and slot ovens, the data of the latter tests were calculated to include any expansion at the top of the charge as well as the lateral expansion. When available, data from tests in which the movable tilted wall was employed were used in averages. Such data were obtained on most of the low-volatile and medium-volatile coals tested.

Mott and Spooner^{161, 165} have used the Koppers "large-scale swelling test apparatus"¹⁷⁶ in a comparative study with other test methods. With the standard apparatus and test procedure, very plastic coals were found to block the holes in the bottom of the retort and thus cause abnormal indications of their swelling and contracting properties. This trouble was "overcome by using a layer of granular firebrick or a piece of iron gauze or a layer of asbestos paper on the sole of the retort, or by perforating the lower portion of the walls of the retort with holes." The use of

100 percent through $\frac{1}{4}$ -inch size coal was advocated.

Measurement of Distortion of Coke-Oven Walls under Pressure. Koppers A.-G. measured the resistance of a specially constructed wall and of a completely solid wall to known applied pressures. Koppers and Jenkner,^{59, 158} who described this work, recognized that expansion pressure data obtained by laboratory methods could be regarded as only relative, because observed pressures were much higher than actual pressures resulting from the same coals when coked in a commercial coke oven. To measure the resistance to pressure that a coke-oven wall was capable of withstanding, these investigators had built a coke oven loaded on top to correspond to the weight of the brick superstructure of a normal coke-oven roof. The wall was constructed of materials commonly used in coke-oven construction and was backed by a layer of fine coke to equalize pressure. Pressure was applied laterally to the side of the wall by a hydraulic press. The same test was made on a completely solid wall. The results of the two tests showed that outward bending of the two walls was the same up to a total pressure of 12,000 kilograms, or 0.13 kilogram per square centimeter; with increased pressure the solid wall bulged less than the coke-backed wall. Contrary to expectations, initial cracks appeared in both walls at a pressure of 0.09 kilogram per square centimeter. The resistance of 0.13 kilogram per square centimeter of the two walls against pressure from the sides was higher than the 0.08 kilogram per square centimeter pressure said to be enough to cause destruction of a coke-oven wall in practical operation. Koppers and Jenkner stated that due account must be taken of the fact that the pressure in coke ovens during the carbonization of expanding coals alternates from

one side to the other, so that the walls are in constant movement.

Variations in the order of magnitude of expansion pressures determined by "laboratory methods" and the actual resistance of a coke-oven wall proved the desirability of conducting measurements in the coke oven itself or under conditions corresponding to those of actual operation.

Expansion-Pressure Measurements in Coke Ovens. Koppers and Jenkner⁵⁹ conducted expansion-pressure measurements directly in the coke-oven chamber. Earlier measurements of temperatures in the coke oven made with thermocouples encased in 1-inch diameter seamless tubes had shown that these tubes were so compressed during the coking of expanding coal that they could be removed from the oven only with difficulty or not at all. With nonexpanding coals the tubes could be withdrawn without difficulty. To measure the expansion pressure of the coal directly in the oven, Koppers and Jenkner used a measuring apparatus consisting of a flat disk diaphragm of 30-centimeter diameter, which was connected by a water-jacketed iron tube and copper piping to a closed vessel. The bottom of this vessel was covered with mercury which led to a mercury pressure gage. The entire apparatus above the level of the mercury was filled with paraffin oil. The iron tube was 235 centimeters long and was surrounded by a jacketing tube of 42-millimeter diameter. Extending in through the iron tube was a thermocouple, which measured the temperature in the center of the disk diaphragm.

The apparatus was introduced, up to the top end of the iron tube, through the charging hole of the coke oven into the freshly charged coal in a plane, so that the sides of the diaphragm paralleled the walls of the coke oven. To correct for the effect of heat on the contained paraffin oil, the

diaphragm had been calibrated previously up to a temperature of 95° C. The iron tube between the diaphragm and the top of the oven was kept at a constant temperature during the test by regulating the flow of cooling water through the jacketing tube. The test could be extended only up to the end of the period of water evaporation in the middle of the coke-oven chamber, namely, up to about half of the carbonizing time. A very strongly expanding coal with a carbonizing time of 28 hours showed pressures up to 0.11 kilogram per square centimeter in an oven chamber 2 meters high. From plant experience this coal was known to cause heavy oven operation and inevitably, after a short time of use, to cause damage to the coke oven. The complexity of such tests and the impossibility of extending them throughout the whole carbonizing period led to their abandonment and to the construction of large-scale installations in which all the phenomena of expansion and expansion pressure that act on the oven walls could be determined for the entire period of coking.

Distribution of pressure in a Becker coke-oven chamber was determined by Agroskin.¹⁸² In a coal charge containing 21 percent volatile matter and 10 to 15 percent moisture the maximum pressure was always observed in the plastic layer and was reached after 3 hours of heating. Pressure was greater near the floor of the oven during the first half of the coking period but decreased during the second half.

Ulrich¹⁸³ described an apparatus that could be placed directly in the coal charge in the coke oven to measure the swelling pressure of the coal charge throughout the

¹⁸² Agroskin, A. A., *Coke and Chem. (U.S. S.R.)*, 9, No. 3, 34-8 (1939).

¹⁸³ Ulrich, F., *Glückauf*, 75, 128-33 (1939); "Investigator," *Coke and Smokeless-Fuel Age*, 1, 98-102 (1939).

entire coking period. Tests were made first in a coke oven at the test station of the Rhenish-Westphalian Coal Syndicate. The horizontal chamber oven had a width of 300 millimeters and a capacity of 120 kilograms of coal. The measuring apparatus was introduced through the charging door above the oven and into the coal, so that the pressure plate was parallel to and equidistant from the oven walls.

Four coals, containing about 17.5, 23.0, 23.5, and 26.0 percent volatile matter (dry basis) and about 8 percent moisture, were each charged at an average bulk density of 720 kilograms per cubic meter and carbonized at a flue temperature of 1,100° C for 12 hours. The maximum pressure values of the 4 coals, in the order given for increasing volatile-matter content, were 0.268, 0.127, 0.093, and 0.078 kilogram per square centimeter. Three other coals containing 19.5, 19.0, and 23.0 percent volatile matter (dry basis) gave 0.150, 0.145, and 0.116 kilogram per square centimeter maximum expansion pressures, respectively. It will be observed that, as the volatile matter of the coals increased, the expansion pressure maxima obtained in the Ulrich apparatus decreased regularly. The same coals tested in a laboratory apparatus showed maximum expansion-pressure values that changed irregularly with the volatile content of the coals and were from 2.43 to 8.46 times larger than those found with the Ulrich apparatus. The greatest differences were observed between tests on coals containing the highest volatile matter.

After the working reliability of the apparatus had been established in the small test oven, further measurements were made with different kinds of coal and under different working conditions in individual coke plants of the Ruhr district. It was found expedient to introduce the measuring apparatus through the oven door at a height of

1.50 meters above the oven sole, and with the measured position at equal distances from the oven walls and at about 1 meter from the door. Two tests on a coal containing 26.8 percent volatile matter, one sample with 8 and the other with 9 percent moisture, were made in an oven chamber 500 millimeters wide, with a heating flue temperature of 1,100° C and coking time of 18 hours. The average deviation in expansion-pressure values between the two tests for readings taken every hour was only ± 0.0056 kilogram per square centimeter. The largest average deviations were observed at 1 hour, 16 hours, and 17 hours. That at 1 hour amounted to 0.11 kilogram per square centimeter and was attributed to the difference of 1 percent in the moisture content of the two charges. The deviation of 0.017 kilogram per square centimeter at 16 hours and of 0.027 kilogram per square centimeter at 17 hours occurred, respectively, when test 1 reached its maximum expansion value of 0.098 kilogram per square centimeter and when test 2 reached its maximum expansion pressure of 0.092 kilogram per square centimeter.

Ulrich studied the effect of different flue temperatures upon the shape of the expansion curve and the magnitude of the maximum expansion pressure. A "strongly swelling" coal containing 23.0 percent volatile matter when carbonized in the test oven at a flue temperature of 1,200° C gave a maximum expansion pressure of 0.34 kilogram per square centimeter after 7.5 hours of coking time. When carbonized at a flue temperature of 1,000° C the maximum expansion pressure was 0.24 kilogram per square centimeter after 10.5 hours' coking time. Both tests showed strong shrinking of the charge after these maxima were reached. A feebly swelling coal containing 23.5 percent of volatile matter, when carbonized in the test oven at heating flue

temperatures of 1,200, 1,000, and 800° C, gave maximum expansion pressures of 0.11, 0.084, and 0.052 kilogram per square centimeter, respectively, at corresponding coking times of 8.5, 12 and 9 hours. The charges showed less pronounced shrinkages than those of the strongly swelling coal.

A strongly swelling coal containing 22 percent volatile matter was tested in a plant oven chamber, 450 millimeters wide, at heating flue temperatures of 1,050 and 930° C. This oven was normally operated at the lower flue temperature to produce as much large coke as possible. When the coal was carbonized at a flue temperature of 1,050° C, its maximum expansion pressure was 0.156 kilogram per square centimeter after 17 hours of coking time; the temperature at the measuring point was 400° C. When carbonized at the flue temperature of 930° C, the maximum expansion pressure was 0.104 kilogram per square centimeter after 20.5 hours of coking time; the temperature of the measuring point was 310° C.

The larger expansion pressures shown at the higher flue temperature in both test-oven and plant-oven chamber were explained by increases in charge density caused by the expansion force resulting from the higher rate of coking which occurred earlier than the counter effect resulting from the shrinking process.

The maximum expansion pressure registered by Ulrich's apparatus of a coal containing 18 percent volatile matter and carbonized at an average flue temperature of 1,050° C in the 300-millimeter test oven was 0.28 kilogram per square centimeter after 10.6 hours' coking. Under similar conditions, in a 540-millimeter commercial coke oven the maximum expansion pressure was 0.16 kilogram per square centimeter after 14.5 hours' coking. Ulrich suggested

that, because of the smaller average coking rate in the wider oven with uniform wall temperatures, a longer time was required for the coal charge to increase in density owing to the expansion, so that the shrinking process set in proportionately earlier, and thus the attainment of the higher maximum expansion pressure capable of being established in the narrower oven was prevented. An alternative suggestion was that the slower rate of carbonization in the wider oven develops a lower plasticity according to the general rule that carbonizing time varies directly with the square of oven width.

Several tests were carried out by Ulrich on coal blends whose individual coals had been studied previously. In contrast to the results found by other investigators in other types of apparatus, *the expansion pressure of the blend itself was found to be the resultant of the pressures of the individual coals in the blend.* Ulrich gave only one example, a blend of 50 percent of a fine coal containing 17.5 percent volatile matter and 50 percent of a coal containing 23.0 percent volatile matter. The blend gave a maximum expansion pressure of 0.164 kilogram per square centimeter after 4 hours' coking; the coal with 17.5 percent volatile matter gave 0.228 kilogram per square centimeter after 5 hours' coking; and the coal with 23.0 percent volatile matter gave 0.118 kilogram per square centimeter after 6.5 hours of coking. If this generalization is borne out by future tests on a large number of blends it opens up an interesting problem of why this should occur in this type of test and not in the older, more widely used tests.

The test data reported by Ulrich indicate that his method should have increased value if more points of pressure in the oven were measured. In discussing this method

Russell¹⁸⁴ pointed out that "The area over which the pressure is measured is an extremely small portion of the area of the oven wall. Determinations of pressure at a number of positions in the oven are necessary in order to obtain a complete survey of the pressures throughout the oven." Unfortunately, Ulrich gave no dimensions of his measuring apparatus. It appears to the writer that in small narrow ovens, particularly, the diameter of the apparatus as well as the volume displaced by the apparatus while in the oven might have a serious influence on conditions of heat transfer. If it should prove practical, the space occupied by the round protection tube could be reduced by the use of one of elliptical cross section, whose major axis is placed parallel to the oven heating walls.

Large-Scale Research Installations for Measuring Expansion Pressure: Two-Sided Heating. It has been recognized for a number of years that test methods using one-sided heating do not simulate the conditions in commercial coke ovens. The sudden increase in pressure observed near the end of the coking period in commercial ovens when the two plastic layers of the coal charge meet does not take place in tests using only one-sided heating.

Important papers^{59, 180, 184, 185} have appeared describing the results of studies made by the Koppers Company in large ovens using two-sided heating. Several laboratories also are adapting two-sided heating to smaller units where the cost and difficulties of carrying out the tests are not so great as to preclude routine testing of coals and blends.

Koppers and Jenkner⁵⁹ measured the

¹⁸⁴ Russell, C. C., *Trans. Am. Inst. Mining Met. Engrs.*, **139**, 313-27 (1940).

¹⁸⁵ Russell, C. C., paper presented before Joint Conf. of Production and Chemical Comm., Am. Gas Assoc., May 23-25, 1938, 4 pp. (mimeographed).

expansion pressure of the coal charge carbonized in a specially designed carbonizing unit. The installation consisted of a vertical coke-oven chamber, heated from both sides by lateral flues and with heating walls that could move independently of each other in frames carried on rollers. The cover of the chamber was provided with an exit for the escape of distillation gases. A hydraulic measuring device was installed against the outside of one chamber wall and fastened to the frame of the other chamber wall. The device was filled with water and contained a main piston and an auxiliary piston. Pressures were read on an attached manometer. The auxiliary piston could be screwed tight, so that the highest pressure developed during the whole of the carbonizing time could be determined without any movement of the oven walls. If, however, it was desired to measure the movement of the walls under pressures above a certain value the auxiliary piston was then loaded with a weight that corresponded to the highest desired pressure. A movement of the walls then took place if the pressure in the hydraulic arrangement exceeded that corresponding to the load on the auxiliary piston. With chosen operating conditions, therefore, either pressure occurring at any time during carbonization of the coal charge or the distance traversed by the wall under a certain pressure on the oven walls could be measured. The progress of temperatures in the coal charge, at the center of the oven, and on the oven walls was followed during the entire carbonization period. Temperature curves constructed from these data showed that the progress of carbonization in the test oven corresponded to practical coke-oven conditions.

The research apparatus recorded pressures generally between 0.1 and 1 atmosphere, although some poorly coking coals

exhibited much lower pressure. Very considerable pressures were set up during the period when the two plastic layers were coalescing, which confirmed the fact that the increased rate of coking here increased expansion pressure. The different order of magnitude of the results obtained with the large-scale research apparatus and with the laboratory method of Damm⁸ was explained by the difference in conditions of carbonization and especially by the difference in width of the plastic layer and the shape of the coke in the two types of test. Some coals that showed temporary expansion in the laboratory test showed no expansion in the test oven, even when a charge of higher bulk density was used. Coals that gave relatively like results by the two methods did not include the strongly shrinking coals that expand temporarily in laboratory tests.

To settle definitely a number of questions relating to the expansion of coal, Koppers and Jenkner⁵⁹ made a series of large-scale tests to determine the relationship between expansion pressure and the following factors: (1) different coals with uniform bulk density; (2) influence of bulk density; (3) influence of carbonizing time; and (4) the influence of admixtures, whereby the coal was made leaner or richer. For (1), a bulk density of 950 kilograms per cubic meter (dry-coal basis) was used, which corresponded to the densest parts of the coal charge in a 4-meter-high oven chamber when using a coal with 40 percent above 2-millimeter size and with 12 to 13 percent moisture. Four coals were tested under closely comparable conditions. The coal that showed the highest expansion pressure, 0.63 kilogram per square centimeter, also gave the highest degree of expansion in the Koppers A.-G. laboratory apparatus. Two other coals gave maximum expansion pressures of 0.43 and 0.35 kilogram per square

centimeter near the end of coking in the large-scale tests but were definitely contracting throughout the laboratory tests. The fourth coal gave no appreciable expansion pressure in the large-scale test but showed a temporary expansion pressure up to 0.43 kilogram per square centimeter and an aftershrinkage of 4 percent in both the Koppers A.-G. and Damm laboratory tests. Moreover, this coal was tested at a lower charge density, 750 kilograms per cubic meter, in the laboratory tests as compared with the higher charge density of 950 kilograms per cubic meter in the large-scale test. The lack of expansion in the large-scale test was explained by the shrinking of the coke, which was first formed near the oven walls. It may be said that a coal showing high expansion pressure in the laboratory with only slight shrinking of the coke after carbonization will, in actual operation, cause greater and more rapid destruction of chamber walls than a coal that gives a smaller expansion pressure in the laboratory but the same shrinking of the coke.

The influence of bulk density on expansion pressure was determined in the large-scale arrangement on a coal that tests in the laboratory apparatus had indicated was harmless. With a bulk density of 800 kilograms per cubic meter of dry coal, no expansion pressure on the oven walls was observed; with an increase to 846 kilograms per cubic meter a slight pressure was noted after the second hour, the maximum expansion pressure, which amounted to nearly 0.1 kilogram per square centimeter, being reached in the fifteenth hour of carbonization. When the coal was carbonized with a bulk density of 913 kilograms per cubic meter, a maximum pressure of nearly 0.3 kilogram per square centimeter resulted at the end of 15.5 hours. With a bulk density

of 964 kilograms per cubic meter a maximum pressure of nearly 1.0 kilogram per square centimeter was obtained in the sixteenth hour of carbonization. It was observed that the maximum expansion pressures all occurred at about the same time, within 4 to 6 hours, in respect to the end of the whole carbonizing times, 18 to 22 hours. These maxima lasted only a short time and decreased in duration with increased bulk density of the coal charge. Longer total carbonizing times were required with greater bulk densities.

The influence of carbonizing time on expansion pressure was determined in the 27- and 18-hour tests in the large-scale installation. Contrary to the laboratory results of Hofmeister,⁶² the amount of expansion did not increase with a reduction in carbonizing time, but with the longer carbonizing period showed a slightly higher maximum expansion pressure, and 6 hours later. However, the bulk density of the coal was 971 kilograms per cubic meter in the 27-hour test, compared to 935 kilograms per cubic meter in the 18-hour test. The 27-hour test also showed greater shrinking near the end of the carbonizing period.

The influence of different coals in a blend on the expansion pressure is a subject of great economic importance. Coals rich in dull coal have been found by Lehmann and Hoffmann¹⁸⁶ to be especially suitable agents to reduce expansion pressure. The use of such coals for blending purposes is economically desirable, therefore, if the blending material must otherwise be shipped in from outside sources. Koppers and Jenkner⁵⁹ determined the influence of crushed, washed nut coal of high dull-coal content upon reduction of the expansion

pressure of a high-expanding coking coal. Under the same carbonizing conditions in their large-scale installation, the maximum expansion pressure of the original expanding coal was reduced from 0.65 to 0.33 and 0.13 kilogram per square centimeter with 20 and 30 percent additions of the washed nut coal, respectively. Quite often, the usual coking coals could be made safe for coking in an oven by the addition of only 10 to 20 percent of a dull coal prepared in accordance with modern petrographic principles, unless the original coking coal had an exceptionally high expansion pressure.

Similar tests showed that about 70 percent of a good-coking, fine, gas-rich coal containing 27.6 percent volatile matter had to be added to the original coal to reduce expansion pressure to the same extent as that caused by a 30 percent addition of nut coal rich in dull coal. The maximum pressure of the blend with gas-rich coal occurred at the end of the third hour of carbonization and continued for 4 hours, whereas that with the dull-coal blend occurred only about 5 hours before the end of carbonization and lasted only a short time. The same high bulk density, around 906 kilograms per cubic meter, was used, and expansion pressures were first shown at the start of the tests with both blends. Pressure increased in the blend with gas-rich coal up to 2.5 hours, after which shrinking opposed the expansion pressure and gradually compensated it up to the end of the test. A blend containing 75 percent of the gas-rich coal showed even greater effects. With the 30 percent addition of dull nut coal the expansion pressure was constant from the third to the fourteenth hour, then rose to a maximum of 0.13 kilogram per square centimeter, and was followed by shrinking. Petrographic analyses by the method of Stach and Kühlwein for coal

¹⁸⁶ Lehmann, K., and Hoffmann, E., *Glückauf*, **67**, 1-14 (1931); *Brennstoff-Chem.*, **13**, 21-9 (1932); *Fuel*, **13**, 271-8 (1934).

slacks¹⁸⁷ of the extremely strongly expanding coal, of the gas coal, and of the nut coal showed, respectively, 89.2, 77.9, and 58.0 percent bright coal, 7.4, 17.1, and 38.4 percent dull coal, and 1.1, 2.8, and 2.5 percent fusain.

Koppers and Jenkner⁵⁹ also determined the influence of 10 percent additions of coke breeze to the same extremely strongly expanding coal. The degree of expansion here was not reduced nearly as much as by the use of dull coal or gas-rich coal under the same carbonizing conditions. The addition of coke breeze to extremely strongly expanding coals in practice, though known to increase the size and hardness of the coke from some coals, has not been as satisfactory as the addition of dull coal to reduce expansion pressure.

The movable-wall coke oven designed and erected by the Koppers Company was described by Russell.^{184, 185} In the first group of tests made with the oven, the wall was allowed to move against a constant pressure of 2 pounds per square inch. The maximum linear movement of the wall produced by a low-volatile Beckley Seam coal, expressed as percentage of the original oven width, was 8.8 percent after 7.75 hours of heating time. The rate of movement increased rapidly for the 15-minute interval immediately before this maximum and then dropped off slightly. The heating wall temperature at the end of the test was 971° C. Tests on the same coal at a bulk density of 55.5 pounds per cubic foot and a constant pressure of 2 pounds per square inch in an Altieri Type A tester¹⁷⁷ showed 12.6 percent maximum linear expansion. The final heating wall temperature was 934° C. When calculated to a bulk density of 54.0 pounds per cubic foot, according to the method of Auvil and Davis,¹⁸¹ the results

by the Altieri tester gave 9.6 percent linear expansion, or within 1 percent of the 8.8 percent expansion at this bulk density found by Russell.

When the movable-wall oven was arranged to measure pressures developed during carbonization, a low-volatile, Beckley Seam coal heated from both walls of the oven showed a maximum pressure against the movable wall of 6 pounds per square inch after 6.5 hours of coking. Near the end of this period pressure rose rapidly to a maximum and then fell rapidly. The curve obtained was comparable, in general, with those described by Koppers and Jenkner.⁵⁹

To prove that the sudden increase in pressure near the end of the coking time was caused by the juncture of the two plastic zones, the oven was then arranged so that it was heated *only from one side*. To reduce the coking time comparable to that used with two-wall heating, the half of the oven space on the stationary-wall side was filled solidly with brick. To prevent the cold stationary wall from absorbing heat from the heated movable wall, the coal space (now half that of the normal oven) was packed with Sil-O-Cel brick until just before charging the coal. The Sil-O-Cel brick were then removed, the door put back and luted, and the coal charged as soon as possible thereafter. This test arrangement allowed heating only from the movable-wall side and, consequently, the formation of only one plastic zone. The maximum pressure now developed was only 4.7 pounds per square inch after about 5 hours' coking. This maximum was approached gradually, and the pressure then fell slowly. The curve had much the same general shape as those obtained in test apparatus in which the volume change is measured and in which the coal is heated from one side.

¹⁸⁷ Stach, E., and Kühlwein, F. L., 64, 841-5 (1928); *Fuel*, 8, 191-8 (1929)

Tests in the Koppers movable-wall oven show a number of advantages over other methods of testing expansion pressure of coals now used in the United States. By heating from two sides, thereby causing the formation of two plastic zones, and measuring the actual pressures developed by the coal against the movable wall, the conditions of coking in a commercial coke oven are more closely simulated. Two-sided heating of low-volatile coals develops a pressure peak at the time of juncture of the two plastic zones. This pressure peak is as much as 40 percent higher than the pressure just before the beginning of this rapid rise, which is that representing approximately the maximum pressure given by one-sided heating. Furthermore, the measurement of the increase in width of the movable-wall oven is obtained throughout the coking period and in the direction in which the coking charge, if dangerous, would produce undesirable pressures. The rate of increase in width of the oven is particularly important in borderline coals. In methods of testing coals that heat only from one side and under a load of 2 pounds per square inch, expansion is measured in terms of linear increase in dimensions (upward movement) of the coal charge. Borderline coals tested under such conditions may develop pressures just under 2 pounds per square inch, and the final volume obtained may indicate slight shrinking. When the coal charge is heated only from one side only one plastic zone is formed, and even the small rapid increase in pressure near the end of the coking period cannot be determined. Consequently, the pressure peak of more than 2 pounds per square inch that would occur with two-sided heating when coal is coked in a full-scale commercial coke oven would not be detected by such methods. A coal tested in the Altieri Type A tester indicated that this borderline coal

would be safe to use in a commercial oven. In the Koppers movable-wall oven the same coal, after 6 hours' coking, showed a pressure against the wall of 2 pounds per square inch; this pressure rose to 4 pounds per square inch at 6.5 hours, and then dropped rapidly. It is assumed that this coal would behave in a similar manner or even produce a greater pressure peak than 4 pounds per square inch in a full-scale oven because the charge here is approximately four times higher than that in the movable-wall oven.

High-volatile coals and various mixtures used regularly in coke-oven plants were tested in the movable-wall oven. None of the high-volatile coals produced a pressure of more than 1 pound per square inch. A few mixtures of high-volatile and low-volatile coals produced pressures as high as 1.5 pounds per square inch. Usually, coals or blends with pressures under 1.5 pounds per square inch did not exhibit a pressure peak near the end of the coking period as did the low-volatile coals. A logical explanation of this difference in behavior seems to be that the maximum fluidity of the high-volatile coals is much higher than that of the low-volatile coals. The high-volatile coals are fluid enough to permit the escape of gas without the creation of high pressures, even at the juncture of the two plastic zones. Measurements of the degree of fluidity in the two classes of coals confirm this explanation.

Carbonization of Low-Rank Coals under High Applied Pressure. The effect of varying the pressure applied during the carbonization of coking coals has been discussed in connection with reviews of test methods and results obtained. It has been shown that pressure up to a certain value, depending upon the particular coal, is necessary to produce a good coke. The influence of applied pressure upon the carbonization

properties of lignites and other noncoking coals is well illustrated by papers by Gauger, Taylor, and Ulmen¹⁸⁸ and by Blayden, Noble, and Riley.¹⁸⁹

Gauger, Taylor, and Ulmen¹⁸⁸ studied the influence of applied pressure on the carbonization of lignites. Samples of lignite, air-dried on a hot plate and ground to various sizes, were carbonized in an iron pipe under pressure applied from each end by means of iron plungers actuated by a Riehle testing machine. The charged sample was first compressed at a preliminary briquetting pressure and then heated slowly in a controlled electric furnace under the desired pressure. Pressure had to be adjusted during the test, as the evolution of volatile products decreased the resistance of the coal to pressure. Temperatures were measured by means of a thermocouple whose hot junction was on the outside of the pipe, and, consequently, were higher than that of the lignite. Heating was continued until the evolution of volatiles had almost ceased, after which the pipe and plungers were removed and the residue was cooled, removed, and examined.

The influence of various factors was studied. It was found that a high initial briquetting pressure (20,000 pounds per square inch) was necessary to obtain a satisfactory product. A minimum coking pressure of 636 pounds per square inch was required at 600° C to produce a suitable coke; higher pressures improved the coke. With a pressure of 1,920 pounds per square inch, excellent cokes were obtained at temperatures as low as 530° C. Twenty-mesh size proved to be superior to 10-mesh size, and air-dried was much better than steam-dried lignite (Fleissner method), for pro-

ducing good cokes. Blending lignite with 3.2 percent of lignite tar gave a good coke at 636° C, although not perceptibly better than that produced from lignite alone. Lignite char blended with 6.25 percent of Pocahontas coal produced a good coke under the usual pressure-carbonization conditions, whereas a 20 percent addition of this coal was needed to give the same results by ordinary heat treatment alone. Variations in coking pressure, from no pressure upward during the test, produced cokes inferior to those formed under otherwise similar conditions but with constant high pressure maintained throughout the test. Grinding and recoking a sample gave an inferior product, indicating that the coking constituents were broken down in the pretreatments. Within certain limits, it may be concluded that the effects of pressure and temperature were complementary in inducing coking of lignites and of mixtures of lignite char with small amounts of a coking coal.

Blayden, Noble, and Riley¹⁸⁹ used as coal container a flat-bottomed, thick-walled, iron vessel, 4 inches in diameter and 4 inches in height, which was provided with an iron piston having a flat head whose center was fixed to the end of a piston tube. The annular clearance between piston head and walls of the vessel was about 1/32 inch. The vessel was heated unidirectionally from below. One hundred grams of coal was placed in the iron vessel and carefully leveled to a layer of uniform thickness. Dry, oxygen-free, nitrogen gas was passed in, and the rate of heating was adjusted as follows: room temperature to 250° C, at 5° C per minute; 250 to 650° C, at 2° C per minute; 650 to 900° C, at 5° C per minute; thereafter the temperature was maintained at 900° C for 20 minutes. Heating was then stopped, and the contents of the furnace were allowed to cool in

¹⁸⁸ Gauger, A. W., Taylor, J. R., and Ulmen, C. W., *Ind. Eng. Chem.*, **24**, 36-40 (1932).

¹⁸⁹ Blayden, H. E., Noble, W., and Riley, H. L., *J. Iron Steel Inst.*, **136**, No. II, 47-62P (1937); *Engineering*, **144**, 385-7 (1937).

the stream of nitrogen. The amount of swelling or contraction of the coal charge during the test was determined from the movement of a lever arm over a scale.

Two Northumberland "noncoking" coals were carbonized under mechanical pressures ranging from 0.2 to 20.4 pounds per square inch. One coal, C57, had been stored for a long time in about $\frac{1}{4}$ -inch size and was probably oxidized slightly. It was ground to pass 60 I.M.M. mesh size and carbonized. The second coal, C518, was freshly mined and was carbonized in four size gradings: $\frac{1}{8}$ - to $\frac{1}{16}$ -inch, 20 to 40 I.M.M., 60 to 100 I.M.M., and through 100 I.M.M. sieves. Special precautions were taken to insure that the several samples were not oxidized, either before or during carbonization. This coal showed temperature ranges of transient swelling when carbonized under the higher pressures, the minimum pressures at which this occurred being lower for the finer grain sizes. All samples of coals C57 and C518 showed a primary contraction, often fairly rapid, between 300 and 450° C, which corresponds approximately to the plastic range of coking coals. This contraction was followed by a relatively slow secondary contraction. The final contraction was taken as the percentage difference between the thickness of the coke layer produced at 900° C and that of the original compressed coal. The observed contractions (primary, secondary, and total) were not straight-line functions of applied coking pressures.

The relative strength of the prepared cokes was determined by a micro strength apparatus devised by the Northern Coke Research Committee (NCRC). For coal C57 marked increases were found in the apparent specific gravities and in the NCRC micro strength indexes of the cokes produced when the applied coking pres-

sure was increased to 10 pounds per square inch; further pressure increases had smaller effects. These were associated with corresponding decreases in total and apparent porosity. The micro strength of the coke made under a pressure of 20.4 pounds per square inch was comparable with that of an average metallurgical coke. Similar phenomena were shown by the several graded sizes of coal C518, although they were modified by the swelling that occurred during carbonization at the higher pressures. The finest size coal produced the strongest coke. Differences in the real specific gravity of the cokes produced at the different applied coking pressures were small. A general parallelism was shown between the above-mentioned properties and "wet" oxidation rates, the specific electrical conductivities, and total contractions measured on these cokes. The cause of the observed influence of applied coking pressure was discussed.

"PLASTOMETRIC INVESTIGATIONS" ON RUSSIAN (U.S.S.R.) COALS

Most of the published investigations by Russian workers on the plastic and related properties of U.S.S.R. coals have been interpreted upon the basis of observed relations between the thickness of the plastic layer and certain other properties of these coals. It should be emphasized that the investigations are based largely upon direct measurement of thickness of the plastic layer. In the experience of the writer, such a measurement is exceedingly difficult to make with certainty. Certain essential details of the description of the method used by the Russian investigators have not been published, so that it has not been practicable to check their results in the U. S. Bureau of Mines laboratories. However, many of the conclusions reached by Russian workers appear reasonable.

The interpretation of the experimental data was based upon the earlier studies of Stadnikoff¹⁹⁰ and of Davies and Wheeler.⁷⁰ According to Stadnikoff, the formation of a well-fused semicoke can occur only if most of the coal material has passed through a liquid state. Sapropelite coals have been formed by oxidation and by polymerization of fatty acids derived from algal fatty oils and are supposed to contain mixtures of fatty acids which are mainly saturated and are regarded as bitumens, polymerized unsaturated acids, and their salts.

The bituminous portion of this class of coals begins to melt at as low as 200° C, but the bitumens do not undergo decomposition up to 400° C and can dissolve the more refractory compounds. At 400° C decomposition and some decrease in solution begin; but in the sapropelite part of the remaining coal depolymerization processes arise, which lead to the formation of relatively fusible products. These products are intermediate between the easily fusible bitumens and the infusible components of the remaining coal. They bring about the solution of the infusible parts of the remaining coal and are themselves decomposed to some degree in the process. The coking power is determined, therefore, by the degree of solution of the remaining coal in the molten bitumens and is proportional to the time the flux exists before the beginning of decomposition with carbonization. According to Davies and Wheeler,⁷⁰ the formation of a uniform coke structure can occur even after the flux begins to decompose and up until the end of its hardening.

Sapozhnikov and Bazilevich¹⁹¹ stated:

¹⁹⁰ Stadnikoff, G. L., *Khim. Tverdogo Topliva*, **2**, Nos. 11-12, 13-27 (1931); *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 674-94 (1931).

¹⁹¹ Sapozhnikov, L. M., and Bazilevich, L. P., *Investigation of the Coking Process; Classifica-*

If we adopt Stadnikoff's point of view and also take into account the data of Davies and Wheeler, the agglutinating power of coal, namely, its ability to give a fused semicoke of uniform structure, should be proportional to the time spent in the plastic state (at some definite rate of heating). In addition, the longer the coal remains plastic the thicker should the plastic layer become during coking. From this point of view, we can expect the caking power to be proportional to the thickness of the plastic layer. . . . The thickness of the plastic layer actually is a measure of the caking power of coal.

These general conclusions were reached in 1935 after several years of experimental work, from which various applications of the data obtained in measurements of the thickness of the plastic layer were made to other data in different classification schemes of Russian coking coals.

Before describing the plastometric method used in Russia for investigating and classifying the U.S.S.R. coking coals and blends, three earlier papers by Sapozhnikov will be summarized briefly. Sapozhnikov¹⁹² determined caking ability, swelling and shrinkage properties, and volatile-matter content of a number of U.S.S.R. coals. These were found to be additive properties, and hence it was possible to predict the kind and proportions of the different coals tested that had to be mixed to produce a good grade of coke. This paper¹⁹² was not available to the writer, but the apparatus used for determining the swelling and shrinkage properties of the coals apparently embodied provision for measuring the thickness of the plastic layer. Sapozhnikov¹⁹² concluded that the difficulties experienced in the operation of

tion of Coals and Calculation of Coking Mixtures on the Basis of the Plastometric Method, State Scientific Publishing House of Ukraine, Kharkov, 1935, pp. 5-33.

¹⁹² Sapozhnikov, L. M., *Domez*, **1931**, No. 9, 72-5; *Chem. Abs.*, **26**, 3362 (1932).

the coke oven and in the removal of the coke were due to irregular coordination between the time of swelling and the time of setting of the coke mass and also to the rough surface of the coke, which prevented its easy removal from the oven. He¹⁹³ found that mixtures of 3 of 4 coals from the Donets Basin, which contained up to 30 percent of the lean (sintering) coal "PS," gave satisfactory operation in fast-working coke ovens. The caking-capacity number of the coal mixtures was kept within the range of 17 to 20, and the elimination of gases was avoided as much as possible after the setting of the plastic mass. Such mixtures had no distinctly pronounced expansion pressures.

Plastometric test methods used so widely in Russia today for measuring various special properties of coking coals were based originally upon either the constant-pressure type of test for measuring swelling or the constant-volume type of test for determining the swelling pressure of coal. Suitable provisions have been introduced in the apparatus and test procedure to permit the determination of selected special properties of the coal charge during its carbonization process.

The familiar plastometric investigation was developed by Sapozhnikov and Bazilevich.^{154, 155, 167, 168, 194} The constant-pressure (Koppers A.-G.) type of apparatus was modified to permit simultaneous measurements of the thickness of the plastic layer and of the linear, vertical expansion and the aftershrinkage, which was termed "final drop" or "final settling" of the coal charge during its carbonization. With but minor changes, the plastometric investigation has been used extensively since 1930

by Russian workers. The following description of the apparatus and test procedure was based upon the literature references just cited.

The cylindrical retort had an inside diameter of 60 millimeters and was provided with a replaceable perforated bottom. The piston head of 58-millimeter diameter contained several vertically drilled holes. The smaller holes permitted escape of gases and vapors. One large hole received an iron tube sheathing a thermocouple, and a second admitted a paper tube surrounding the calibrated plastometer needle used to measure the thickness of the plastic layer. The piston rod was connected at the top to the usual weighted lever arrangement. The free end of the longer lever arm carried a pen that recorded, on a revolving drum, the linear expansion and contraction of the coal charge during its carbonization.

Before the test was started, the retort was carefully cleaned, its walls were lined with filter paper, and its bottom was covered with an asbestos disk. The iron and paper tubes were placed vertically in proper positions relative to the holes provided for them through the piston head. The retort was then charged with 100 grams of air-dried, minus 1.5-millimeter coal. The charge was leveled off and lightly tamped to a height of 50 to 45 millimeters and, apparently, to a void space of 40 percent. The coal charge was covered with an asbestos disk provided with two holes concentric with the two holes in the superimposed piston head to receive the iron and paper tubes. The top of the piston rod was then attached to the lever, and the loading weight on the longer arm was adjusted so as to apply a pressure of 1 kilogram per square centimeter on the top surface of the coal charge. The thermocouple and plastometer needle were inserted in their respective tubes, and the as-

¹⁹³ Sapozhnikov, L. M., *Khim. Tverdogo Topliva*, **2**, No. 10, 68-77 (1931).

¹⁹⁴ Stadnikoff, G., *Analysis and Testing of Coal*, State Publishing House, Moscow, 1936, pp. 98-106.

sembled retort and its contents were placed in an oven heated electrically from the bottom by means of a Silite rod.

Starting at 240 to 250° C, the temperature rose at a rate of 3° C per minute. Because of the paper insulation on the inside walls of the retort and the poor conductivity of the coal, heating took place unidirectionally from the bottom of the charge. Thus, complete reproduction of the coking process in an industrial coke oven was claimed. In 4 hours the temperature of the bottom layer of the charge reached 700 to 800° C and that of the top layer 500 to 600° C.

The plastometer needle was graduated in millimeters so that it read zero when its tip rested on the bottom of the retort; when the needle was raised vertically the graduations showed the distance of the tip from the bottom. Before the coal began to soften, the lower end of the paper surrounding the plastometer needle became charred, thereby allowing the plastic coal to flow into the space around the needle point, tending to force it upward. By carefully raising the needle it could be determined whether its tip was sticking to the bottom of the retort, which meant that the coal here had become plastic. The corresponding reading of the thermocouple indicated the softening temperature of the coal. With increase in temperature and further penetration of heat into the coal charge the thickness of the plastic layer increased to a maximum and then decreased somewhat.

The plastic coal by flowing into the space around the point of the plastometer needle came into contact with cold air entering the paper tube, and (possibly owing to oxidation) the top surface of the plastic layer became coated with a thin, dense film. This film or crust was said to be strong enough to support the weight of the

plastometer needle and also an additional pressure of light tapping. When the tip of the needle rested on this crust, its distance from the bottom of the retort defined the upper surface or top level of the plastic layer. Light pressure applied vertically to the upper end of the plastometer needle caused the tip of the needle to pierce the film and penetrate easily through the plastic layer of the coal charge until the tip came to rest on the top surface of the semicoke below. The plastometer needle, even under heavy pressure, would not penetrate the semicoke, whose top level, therefore, was defined as the lower surface or bottom level of the plastic layer. The vertical distance between the measured upper and lower surfaces of the plastic layer gave its thickness in millimeters and was determined periodically during the test. The values obtained were plotted later on the millimeter chart paper removed from the drum, which already showed the automatically recorded linear (vertical) changes of the coal charge during the test period.

The completed chart, therefore, included three curves: (a) the volume or expansion-pressure curve indicating the linear expansion and aftershrinkage ("final drop" or "final settling") of the charge; (b) the curve showing the course of the measured heights of the upper surface of the plastic layer from the bottom of the retort; and (c) the curve similarly defining the lower surface of the plastic layer. All three curves were plotted to the same abscissa scale to represent corresponding times and temperature points, the temperature being measured at the bottom of the retort. The ordinates for curve *a* gave the linear expansion and contraction of the coal charge in millimeters with reference to the zero or null line; those for curves *b* and *c* indicated, respectively, the distances in

millimeters of the corresponding upper and lower surfaces of the plastic layer from the bottom of the charge or base of the retort. In the numerous applications of such measurements, the final drop of the expansion-pressure curve (aftershrinkage or final settling of the semicoke), index x , was plotted as the abscissa (reading from right to left), and the maximum thickness of the plastic layer, index y , as the ordinate, in the various classification diagrams of U.S.S.R. coals.

Bazilevich¹⁹⁵ later changed the plastometer needle of the original apparatus¹⁶⁸ into a combined, thin plastometer needle and thermocouple. The temperature of softening at the top level of the plastic layer and the temperature of solidification at the bottom level of the plastic layer could then be determined simultaneously with the corresponding height of these two surfaces measured from the bottom of the retort. It was claimed that the rate of coking did not affect appreciably the temperature limits of the plastic layer.

Poputnikov¹⁹⁶ modified the test apparatus of Sapozhnikov and Bazilevich¹⁶⁸ by using a refractory container for the coal charge and a special device for heating. A constant temperature was then maintained. Analytical data and details of the method were given. A critical study of this and eight other Soviet methods of determining the coking properties of coal was made by Shevchenko,¹⁹⁷ who concluded that the test method of Poputnikov¹⁹⁶ was the most reliable.

Moisik¹⁹⁸ increased the thickness of the plastic layer of coal, thereby slightly en-

hancing its coking properties, by subsection of the coal to high-frequency discharge ($\lambda = 2$ millimeters).

Apparently, the constant-volume type of apparatus used by Russian workers for determining the expansion pressure of coal was designed originally by Sapozhnikov and Bakun.¹⁹⁹ Their papers were not available to the writer. Incomplete descriptions of the apparatus and test procedure have been given by Sapozhnikov and Cherkasskaya²⁰⁰ and by Sapozhnikov.¹⁵⁵ According to the two last references, the retort had a solid bottom, was of "standard" dimensions (apparently, those of the constant-pressure retort), and was hermetically sealed on the top by means of a lid. A 100-gram charge of 0- to 1.5-millimeter size coal was heated at a rate of 3° C per minute up to 700° C. The expansion pressure of the coal was transmitted through a piston passing through the lid to a hydraulic reservoir and was measured by an attached spiral manometer gage.

CLASSIFICATION OF U.S.S.R. COALS

Sapozhnikov²⁰¹ used the measured maximum thickness of the plastic layer of coal as one coordinate in various classification diagrams of U.S.S.R. coals. Usually, for suitable classifications of different types of bituminous coals, the second coordinate had to be supplemented by other factors that characterized the plastic state of these coals. For example, rich gas and coking coals whose thicknesses of plastic layers were comparable but whose contents of

¹⁹⁵ Bazilevich, L. P., *Coke and Chem. (U.S.S.R.)*, **3**, No. 1, 30-41 (1933).

¹⁹⁶ Poputnikov, F. A., *Khim. Tverdogo Topliva*, **7**, 497-502 (1936); *Chem. Abs.*, **31**, 2778 (1937).

¹⁹⁷ Shevchenko, E. P., *Zavodskaya Lab.*, **7**, 610-12 (1938); *Chem. Abs.*, **32**, 9442 (1938).

¹⁹⁸ Moisik, M. R., *Coke and Chem. (U.S.S.R.)*, **6**, No. 9, 24-7 (1936); *Chem. Abs.*, **31**, 7224 (1937).

¹⁹⁹ Sapozhnikov, L. M., and Bakun, N. A., *Coke and Chem. (U.S.S.R.)*, **2**, No. 9, 63, No. 11, 73-8 (1932).

²⁰⁰ Sapozhnikov, L. M., and Cherkasskaya, E. I., *Khim. Tverdogo Topliva*, **6**, No. 2, 100-6 (1935).

²⁰¹ See pp. 34-54 of ref. 191; see also refs. 154 and 155.

volatile matter differed widely fell into different areas of the classification diagram, when these two properties were plotted against each other. However, if the yields of volatile matter were supplemented by certain other factors that defined the rate of release of volatile matter during the plastic state, and if the resultant effects on the expansion and contraction of the coal charge were considered, a more rational differentiation of the properties of different types of coal was obtained.

A number of the special properties of the plastic layer have been investigated for many different types of coal by Sapozhnikov and his coworkers and by other Russian investigators. The data obtained have been plotted as supplementary information on various individual "plastometric diagrams." These individual diagrams all employ the same coordinates, namely, maximum thickness of plastic layer in millimeters as ordinates plotted against final drop of the expansion pressure curve ("final settling" or aftershrinkage of the semicoke) in millimeters, increasing from right to left, as abscissas.

For convenience in discussing the data obtained in the more important published investigations of the special properties of U.S.S.R. coals these individual diagrams have been reproduced here in a composite diagram, Fig. 11. The coordinates of Fig. 11 are in the units generally used in the various charts constructed from data of individual Russian investigations. The curves, lines, shaded area, and points in the body of the diagram have been lettered or numbered for convenience in discussion. A general explanation will be given first of the meaning of the numbered small circles, of the lettered curves and lines, and of the shaded area shown in the body of the composite diagram. With these as guides, the general application and wide usefulness of

the composite diagram representing various proposed schemes of classification of U.S.S.R. coals based upon their experimentally determined special properties will be presented.

Expansion Pressures. The numbers beside the small circles in Fig. 11 designate the measured maximum expansion pressures in kilograms per square centimeter of representative U.S.S.R. coals having the coordinates indicated. The expansion pressures increase in the direction from the lower left corner to the upper right corner of the classification diagram. Coals below the dashed-line curve *kl*, inclined to the right, do not show expansion pressures during carbonization. Coals in the central part of the diagram between curves *kl* and *gh* show expansion pressures between 0.15 and 0.3 kilogram per square centimeter. Coals on the right-hand side and above the curve *gh* show expansion pressures of 0.3 to 2.0 and more kilograms per square centimeter, and their cokes give only small lateral shrinkage. The approximately parallel curves divide the coals of like expansion pressures into separate areas. The heavy curve *gh* is designated as the limit for coals "dangerous due to swelling pressure." Coals above and to the right of this line, when coked alone, may seriously damage the coke oven; they almost invariably lead to "hard pushing" and, in high-speed ovens, even to "mass boring" into the oven walls. Curve *ij* is the limit inside which it is recommended that blends for high-speed ovens (with a coking period of 16 to 18 hours) be kept, and even near this curve symptoms of hard pushing may appear.

Coke Properties. Curve *kl* is approximately the boundary limit between coals or blends that give dusty, easily broken cokes (below) and those that produce well-fused cokes (above). These properties, of course, do not change sharply at this

"boundary limit for dusty cokes," and the change is only gradual as one approaches or moves away from this curve. The resistance to degradation of cokes, defined as the remainder in the Sundgren drum test,

large, little-fissured cokes (below). Within the strip itself fall coals of both properties that may be differentiated among themselves by the aid of supplementary information.

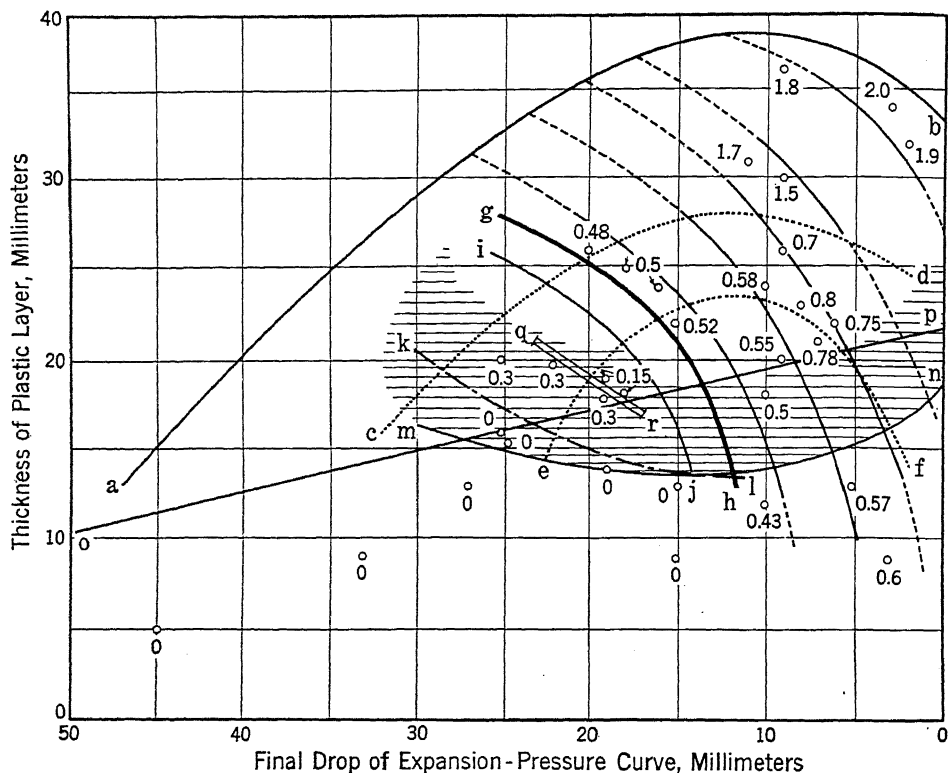


FIG. 11. Classification diagram for U.S.S.R. coals.¹

is around 280 kilograms below curve *kl*, increases to 320 kilograms along the "line of best coking mixtures," *qr*, and reaches 340 to 350 kilograms above the curve *gh*. A properly composed blend must lie preferably above the line *qr*.

The convex upward strip between the dotted curves *ef* and *cd* is the "fissured coke strip." It separates coals that, when coked alone, give brittle, small, fissured cokes (above) from coals producing strong,

The triangular area of the diagram defined by the intersections of curves *kl*, *cd*, and *ij* contains those coals that, when coked alone, give strong, normally fused coke without danger of hard pushing or boring. This area, therefore, is the coking region of the classification diagram and contains coking coals and properly proportioned coking blends. The straight line *qr*, which occupies a central position in the coking region, is the line of best coking mixtures.

It should be observed that in direct plastometric tests of blends containing different kinds of coals the screen analysis of the charged sample has an important effect on the shrinkage of the coke. The shrinkage decreases with increase in size of grain of the samples. Blends with a shrinkage of 18 millimeters or less are to be avoided, because a small change in the proportions of coals in the blend or a fluctuation in the coking characteristics of such a blend may easily move it to the hard pushing limit.

That part of the coking region to the right of curve *ef* assures a large, strong coke, whereas those coals within the fissured strip are not always able, when coked alone, to give a coke sufficiently large and free of fissures. The tendency of such a coal to give a small, fissured coke can be detected from the zigzag expansion-pressure curve with a large rise and fall that accompanies a strongly fissured coking layer. Coals of this kind lie to the left and both above and below the triangular coking region.

The position of the 178 samples²⁰¹ of Donets and Kuznetz coals and blends studied by the plastometric investigation up to 1935 lay below the arc-shaped demarcation line *ab*.

Oxidation. The effect of increasing the degree of oxidation of a coal is to move it toward the lower left corner of the classification diagram. In other words, the thickness of the plastic layer decreases and the final drop of the expansion-pressure curve increases as the coal undergoes oxidation.

Division of Gas Yields. Coals lying above the shaded strip in Fig. 11 give off a much greater volume of primary decomposition products (one coal gave 85.5 percent of the total) from the hot than from the cold side of the plastic layer.

All these coals give a hump-shaped swelling-pressure curve, the rise being greater the further the coal is above this shaded strip.

The coals within the shaded strip give off nearly equal volumes of gas from the hot and the cold sides of the plastic layer, although the gas comes off in spurts and periodically from one side and then from the other. These coals are characterized by zigzag swelling-pressure curves.

The coals lying below the shaded strip give off a greater volume of primary decomposition products from the cold side than do the preceding two types of coal. One coal gave 62 percent from the cold side. The swelling pressure curves of these coals are straight and differ primarily in the magnitude of the continuous drop.

Fluidity. The coals below the straight line *op* form a very viscous layer and do not extrude at all from the side opening in a retort. Passing this line upward, the coals at once show fluidity, which increases rapidly with increase in distance from this line. The coals in the left part of the diagram above this line flow more rapidly than those in the right part of the diagram.

Gas Permeability. Below curve *mn* are the coals having a plastic layer through which gases pass under a pressure of less than 1 atmosphere. Above this curve the resistance to gas permeability increases at once and reaches a pressure of 50 or more atmospheres.

APPLICATIONS OF THE COMPOSITE DIAGRAM

The wide usefulness of the composite diagram as a convenient scheme of classification of Russian coking coals according to their determined properties is well illustrated by data obtained in investigations, which are summarized below.

General. Using experimental data expressed in the same coordinates as those

PLASTIC PROPERTIES OF COALS

of the composite diagram, Sapozhnikov^{154, 155, 202} found that coals of the U.S.S.R. could be arranged in fair order to show a number of regularities in distribution of properties for given areas of the classification diagram. The temperatures of solidification of the various coals all lay within close limits around 475° C. The higher the coal was on the classification diagram, that is, the greater the thickness of the plastic layer, the lower was its softening temperature. Consequently, coals with the longer plastic temperature ranges fell in the upper portion of the classification, or composite, diagram. Coals with thin plastic layers (0 to 17 millimeters) and high shrinkages of their cokes (14 to 45 millimeters) had zero expansion pressures; coals with average (17 to 20 millimeters) plastic layers and average (15 to 25 millimeters) shrinkages of their cokes had expansion pressures of about 0.15 to 0.3 kilogram per square centimeter; and coals with thick plastic layers (25 millimeters or more) and low shrinkages of their cokes (less than 14 millimeters) had expansion pressures above 0.3 kilogram per square centimeter.

Sapozhnikov^{154, 155, 203} observed that coals in the right-hand part of the classification diagram (abscissas less than 15 millimeters) formed a highly cross-fractured coke, if carbonized alone. Coals toward the left part of the diagram (abscissas greater than 22 millimeters) produced a lenticular coke with a high degree of longitudinal fracture. Coals in the central part of the diagram formed coke of normal shape and low fracture; the extent of fracture increased with increase in thickness of the plastic layer.

²⁰² Sapozhnikov, L. M., *Trans. Mendeleev Congr. Theor. Applied Chem., 6th Congr., 1932, 2, Pt. II, 375-9 (1935).*

²⁰³ Sapozhnikov, L. M., *Dnepropetrovsk Coal Research Institute, Bull. 1, 34-54 (1935).*

Properties of Coal Blends. Sapozhnikov and Bazilevich^{154, 204} used coordinates representing individual coals in the classification diagram to calculate the properties of coal blends. The ordinates (maximum thickness of the plastic layer, in millimeters) and the abscissas (final drop of the expansion-pressure curve, in millimeters) for each constituent coal were read from the diagram. With these values and the percentages of the individual coals used in the blend, the location of the coordinates on the diagram for the blend could be calculated. This calculation was possible because of the following properties of the classification diagram.

The thickness of the plastic layer, Y , of a mixture of coals is an additive property that can be calculated for any number of component coals, A, B, C , etc., according to the equation

$$Y_{A, B, C, \dots N} = \frac{\{Y_A \cdot \%A + Y_B \cdot \%B + Y_C \cdot \%C\} + \dots + Y_N \cdot \%N}{\%A + \%B + \%C \dots + \%N} \quad (1)$$

The equation may be simplified by substituting corresponding proportions for the respective percentages of the different coals in the blend.

The abscissa of a binary mixture changes according to a chain line with the convexity directed toward the left of the classification diagram. The length of this chain (or "coking curve") between coordinates on the diagram representing two coals can be calculated according to the "corrected equation"¹⁵⁴

$$S_{AB} = \sqrt{(X - x)^2 + (Y - y)^2} + 3.5 \frac{(Y - y)}{X + 0.2x} \quad (2)$$

²⁰⁴ Sapozhnikov, L. M., and Bazilevich, L. P., *Coke and Chem. (U.S.S.R.), 4, Nos. 5-6, 13-21 (1934); see also pp. 55-68 of ref. 191.*

where X and x represent the greater and smaller abscissas, and Y and y the greater and smaller ordinates, respectively.

Sapozhnikov¹⁵⁴ did not state how the shape of the chain line was established. It could, of course, have been determined by drawing a smooth curve through experimentally determined coordinates for a sufficient number of differently proportioned blends of the two component coals A and B . Or, perhaps, if equation 2 has general application, substitution of the known values of the coordinates for coals A and B into equation 2 and solving will give a definite length for the chain line. It should then be possible to establish mathematically the shape of the chain line which trial calculations have shown is neither a catenary nor a cycloid.

Sapozhnikov¹⁵⁴ gave three examples to show the applications of equations 1 and 2 in the calculation of the coordinates of blends containing 2, 3, and 4 component coals. Given 4 coals, A , B , C , and D , with ordinates of 10, 20, 20, and 40 millimeters, respectively, and corresponding abscissas of 10, 15, 23, and 10 millimeters. Suppose a binary blend of 30 to 20 parts (or 60 to 40 percent) of A and B , a ternary blend of 30 to 20 to 20 parts of A , B , and C , respectively, and a four-component blend of 30 to 20 to 20 to 30 parts of A , B , C , and D , respectively, are to be made.

For Binary Blends of A and B . The length of the chain line or "coking curve," AB , is found by substituting in and solving equation 2,

$$\begin{aligned} S_{AB} &= \sqrt{(15 - 10)^2 + (20 - 10)^2} \\ &\quad + \frac{3.5(20 - 10)}{15 + 0.2(10)} \\ &= \sqrt{5^2 + 10^2} + \frac{3.5 \cdot 10}{15 + 2} \\ &= 11.2 + 2.1 \\ &= 13.3 \text{ mm} \end{aligned}$$

On this coking curve (chain line, AB) will be located mixtures of component coals A and B in all possible proportions. For any given ratio of A to B the ordinate of the binary blend is calculated by substituting appropriate Y values (ordinates) and proportions of coals A and B into and solving equation 1. Thus, in a binary blend of coals A and B in the proportion 30 to 20 (60 to 40 percent), respectively, the value of the ordinate is

$$\begin{aligned} Y_{A, B} &= \frac{10 \times 30 + 20 \times 20}{30 + 20} \\ &= \frac{300 + 400}{50} = 14 \text{ mm} \end{aligned}$$

The point of intersection [m_1] of the ordinate 14 millimeters with the coking curve AB corresponds to an abscissa value of 1.5 millimeters.

For the Ternary Blend of A , B , and C . The value of the ordinate is

$$\begin{aligned} Y_{A, B, C} &= \frac{10 \times 30 + 20 \times 20 + 20 \times 20}{30 + 20 + 20} \\ &= 15.7 \text{ mm} \end{aligned}$$

Since the proportions of coals A and B to each other here remain the same as in the binary blend the equation may be simplified to read

$$\begin{aligned} Y_{A, B, C} &= \frac{14(30 + 20) + 20 \times 20}{30 + 20 + 20} \\ &= 15.7 \text{ mm} \end{aligned}$$

The point of intersection [m_2] of the ordinate with the m_1C coking curve corresponds to an abscissa value of 20 millimeters.

For the Four-Component Blend of A , B , C , and D . The value of the ordinate is

$$\begin{aligned} Y_{A, B, C, D} &= \frac{10 \times 30 + 20 \times 20 + 20 \times 20 + 40 \times 30}{30 + 20 + 20 + 30} = 23 \text{ mm} \end{aligned}$$

or, alternatively,

A, B, C, D

$$\frac{15.7(30 + 20 + 20) + 40 \times 30}{30 + 20 + 20 + 30} = 23 \text{ mm}$$

Sapozhnikov gave the value of the ordinate here as 20 millimeters, which corresponded to an abscissa value of 21 millimeters. [Note: Both the calculation and the drawn curve given by Sapozhnikov appear to be in error.]

Sapozhnikov, Finkelstein, and Cherkasskaya²⁰⁵ obtained data with the plastometric apparatus^{154, 168, 194} on the 70 : 30, 50 : 50, and 30 : 70 blends of four pairs of U.S.S.R. coals. The plotted data¹⁵⁵ showed: (a) that coals with thin (0 to 12 millimeters) plastic layers and large (14 to 45 millimeters) aftershrinkages of their semicokes had zero expansion pressures (lower left part of diagram); (b) that coals with average (12 to 20 millimeters) plastic layers and average (15 to 25 millimeters) aftershrinkages of their semicokes gave expansion pressures of about 0.15 to 0.3 kilogram per square centimeter (center of diagram); and (c) that coals with higher expansion pressures arranged themselves along curves parallel to the upper boundary of the coking region of the diagram (center of diagram upward and to the right).

The (a) group of coals were not fluid, and their thin plastic layers offered no resistance to gas passage. The small amount of liquid developed inside the grains of coal was fused out on their surfaces in very thin films, which struck the grains together and limited their mobility. However, there was not enough liquid to hold back the gases, and the plastic layer remained permeable to them. The (b) group of coals

developed considerable fluidity in the plastic mass, which remained permeable to gases until enough liquid was produced to fill all spaces between the particles. Further increases of 5 to 8 millimeters in thickness of the plastic layer increased the resistance to gas passage.

The (c) group of coals included two types. Those with thin plastic layers and small aftershrinkage, in the lower right corner of the diagram, developed a high expansion pressure, namely, 0.5 to 0.6 kilogram per square centimeter. The grains of these coals were only slightly adhesive and had so little mobility that they did not stick together in a continuous film under the action of high pressure pressing them together from the inside; spaces remained between the grains, which permitted gases liberated on the hot side to pass without appreciable resistance through the plastic layer. The second type of coal, with thicker plastic layers and a wider range of shrinkage, contained grains which became increasingly soft and mobile. The softened grains were swollen by the gas that accumulated inside and so were pressed into each other more and more closely, the free spaces between becoming smaller and smaller. As the plastic layer became thicker, the soft grains finally formed a continuous viscous film impermeable to gases. The plastic layer became fluid only after its thickness had increased 5 to 6 millimeters above that required for gas permeability. The fluidity of the plastic layer increased slowly as the thickness of the layer increased. Coals of the (c) group were coked by the softened grains growing together along their contact surfaces, while neighboring grains were pressed into one another by gaseous decomposition products that accumulated inside the grains.

²⁰⁵ Sapozhnikov, L. M., Finkelstein, P. K., and Cherkasskaya, E. I., *Khim. Tverdogo Topliva*, 6, No. 4, 324-31 (1935). See also ref. 155.

Sapozhnikov^{155, 206} found that only the "fat" petrographically homogeneous coals, in the right part of the classification diagram, when carbonized, give a "homogeneous structureless mass." All other kinds of coal retained the outlines of the initial grains of coal after passing through the plastic period. Therefore, carbonizing blends consisting of coking coals, low-volatile coals, and gas coals are coked not by mutual solution of the various components but by the grains growing out and sticking together at their contact surfaces. At the same time, the processes that go on within the separate grains depend but very little on the presence of neighboring grains of other components of the blend.

The interrelation between grains of the various components of coal blends was studied²⁰⁶ by determining the plastic intervals (temperature difference between softening and solidification temperatures) for the blended coals and plotting these values against the percentage composition of the blends. Blends of two coals in the proportions of 25 : 75, 50 : 50, and 70 : 30 were studied for three pairs of coals.

The first pair of coals, in the right part of the classification diagram—one with a contraction of 1 millimeter and a plastic layer thickness of 34 millimeters and the other with a contraction of 4 millimeters and a plastic layer thickness of 9 millimeters (therefore, of higher softening temperature)—when blended, showed plastic intervals that changed according to a straight-line law. The solidification temperatures of these blends rose as the proportion of the second coal increased, confirming the assumptions made about the softening and growing together of the grains of the coals in the right part of the classification diagram.

When blends were made of two coals, one in the right and one in the left part of the classification diagram, the curves showing the plastic interval plotted against the percentage composition of the blends were entirely different. A series of blends consisting of one coal with a contraction of 2 millimeters and a plastic layer thickness of 32 millimeters and a second coal with a contraction of 25 millimeters and a plastic layer thickness of 12 millimeters showed reductions in the plastic interval with increasing proportions of the second (higher-softening) coal, but the changes were not additive. The curve showed two distinct bends: one where the first coal predominated, and the other where the second coal predominated in the mixture. Each of the coals passed separately into the plastic state.

Blends of a third pair of coals—one in the right part of the diagram with a contraction of 6 millimeters and a plastic layer thickness of 17 millimeters, the second in the left part of the diagram with a contraction of 34 millimeters and a plastic layer thickness of 24 millimeters—also gave a curve with two distinct bends. In this pair the second coal had the lower softening point, and the plastic interval increased as the proportion of this coal in the blends was increased. It may be concluded that coals from the right and left parts of the diagram, when blended, behave like a mixture of heterogeneous substances whose grains do not grow together to form a homogeneous mass of coke.

Effect of Heating Rate. Sapozhnikov and Pashkevich²⁰⁷ studied the effect of heating rates of 3, 5, and 10° C per minute on aftershrinkage of the semicoke. The method was the usual plastometric investi-

²⁰⁶ Sapozhnikov, L. M., *Coke and Chem. (U.S.S.R.)*, 8, No. 10, 10-7 (1938).

²⁰⁷ Sapozhnikov, L. M., and Pashkevich, A. Z., *Khim. Tverdogo Topliva*, 6, No. 3, 202-6 (1935). See also ref. 154.

gation. With increased heating rates, coals with shrinkage indexes of less than 20 showed a marked decrease in shrinkage, whereas those with indexes over 20 increased slightly. Coals in the former group (in the right part of the plastometric diagram) under the normal heating rate of 3° C per minute yielded coke with sharply developed cross fissures, whereas those of the left part of the diagram formed coke with fissures in the longitudinal direction and a prismatic structure. When the coking process was accelerated by heating, the effect on a blend was to move it to the right in the diagram, thereby causing increases in expansion pressure and cross fractures of the coke. To avoid difficult pushing of the coke from the oven, the proportions of the two coals had to be then adjusted to give a shrinkage larger than 20 to 25 millimeters. Cross fracture was reduced also by increasing the proportion of the coal in the left part of the diagram to produce greater shrinkage of the blend. Coke from finely ground mixtures (90 percent through 3 millimeters) could be pushed from the oven, even if the shrinkage was small; that from coarsely ground mixtures, although composed of the same coals, had to show a shrinkage between 21 and 24 millimeters in the plastometric test before the coke could be pushed from the coke oven.

Pashkevich²⁰⁸ found that the fissuring of coke could be reduced appreciably by a rational heating program, even when coking was carried out very rapidly. For rapid coking, the rate of heating should be reduced at the start and increased toward the end of the coking process.

The method of Sapozhnikov and Pashkevich²⁰⁷ was later modified by Kushnare-

vich²⁰⁹ to insure heating at a higher temperature. The coal charge was insulated on top with five 1-millimeter-thick layers of asbestos; the outside of the retort was covered with asbestos paper, and its inside walls were lined to a greater height (55 millimeters, as compared with 50 to 45 millimeters). Heating was carried up to 1,100° C, after which the lever arrangement was attached and the test continued until the expansion-pressure curve became horizontal.

Properties of Oxidized Coals. Kucherenco²¹⁰ found that Donets coal, after oxidation in the laboratory at 140° C with oxygen or under natural conditions in piles in air gave similar results. The Meurice agglutinating numbers were (a) for unoxidized coal, 19; (b) after 1.5 hours in oxygen, 18; (c) after 3 hours in oxygen, 18; (d) after 10 hours in oxygen, 17; (e) after 2 months in air, 19; and (f) after 4 months and 10 days in air, 18. The thicknesses of the plastic layers were (a) 27, (b) 20, (c) 14, (d) 10, (e) 19, and (f) 11 millimeters; the pressures of swelling at constant volume of coal were (a) 0.9, (b) 0.45, (c) 0.03, (d) 0, (e) 0.42, and (f) 0.05 kilogram per square centimeter; and the depressions of the swelling pressure curves were (a) 8, (b) 18, (c) 28, (d) 34, (e) 18, and (f) 35 millimeters, respectively.

Sapozhnikov and coworkers²¹¹ also employed the "plastometric investigation" to determine change in coking properties of coals caused by oxidation. The coordinates of the fresh coals investigated fall in the upper right part of Fig. 11, that is,

²⁰⁹ Kushnarevich, N. R., *Coke and Chem. (U.S.S.R.)*, 7, No. 7, 61-6 (1937).

²¹⁰ Kucherenco, N. A., *ibid.*, 3, No. 12, 63-5 (1933).

²¹¹ Sapozhnikov, L. M., and Kucherenco, N. A., *Coke and Chem. (U.S.S.R.)*, 4, No. 8, 50-8 (1934). See also ref. 154 and pp. 69-89 of ref. 191.

²⁰⁸ Pashkevich, A. Z., *Coke and Chem. (U.S.S.R.)*, 6, No. 8, 37-43 (1936).

above curve *gh*. With increasing oxidation, the coordinates moved in a straight line through the center and to the lower left part of the diagram. Oxidation for 2 to 3 months in open air was enough to bring about the complete change. The authors stated that the southern U.S.S.R. coke plants use oxidized, rich gas coals for blending purposes, instead of the deficient coals in the lower left part of the classification diagram. The equations developed by Sapozhnikov and Bazilevich,^{154, 204} were used to establish the coordinates of blends made of oxidized and other coals.

Coal Beds. Sapozhnikov and Eidel'man²¹² used the plastometric investigation in a study of the changes of properties of coal with the extension of the coal bed. Coals from four typical beds in the principal Donets industrial districts were investigated. The gas coals from these beds gave coordinates lying in the left part (abscissas 30 millimeters and more, ordinates up to 20 millimeters) of the classification diagram. With rich coals the abscissas decreased to about 10 millimeters and the ordinates increased up to a certain maximum, 25 millimeters or more, depending on the coal bed. With coking and lean coals the abscissas continued to decrease and the ordinates dropped rapidly. Such data were used as a guide for locating new shafts to mine coals of certain coking properties.

Petrographic Composition. Correlation of the petrographic composition of coals from the Don Basin with their plastometric coordinates has been made by Kovalev and Eidel'man¹⁵⁴ and of coals from the Kuznetz coal field by Ergol'skaya and by Strongin and Taits.²¹³ The dull coals

were located toward the left part of the classification diagram, the bright coals toward the right part, and the semibright coals (clarains) between.

Podbel'skiĭ and Mosina²¹⁴ found that Ossinovo Seam coal (Kuznetz Basin) showed very high coking power and high swelling pressure. On account of its high vitrain content (average 88.2 percent), some samples gave no shrinkage on carbonization, and others rarely exceeded 6 millimeters.

Volumetric Gas Yield on Cold Side of Charge. Sapozhnikov and Cherkasskaya²¹⁵ established a general relationship between the thickness of the plastic layer and the percentage by volume yield of volatile products evolved toward the colder side of the heated coal charge. The volumes of volatile products evolved on both the cold and hot sides of the charge were determined, although the latter was found to have but little relation to the thickness of the plastic layer.

The apparatus used originally²¹⁵ was that designed by Bakun.²¹⁶ Test conditions were similar to those in the usual plastometric investigation. Readings were made of (a) temperature, (b) volume of gas liberated from the cold side, (c) volume of gas liberated from the hot side, and (d) swelling pressure every 5 minutes to 700° C and thereafter at this maintained temperature until successive gas-volume readings did not differ by more than 40 to 60 cubic centimeters. The volumes of gases (b) and (c), in liters, were plotted as ordinates against temperatures (a), or

gol'skaya, Z. V., *Khim. Tverdogo Topliva*, **8**, 97-108 (1937).

²¹⁴ Podbel'skiĭ, G. N., and Mosina, T. L., *Khim. Tverdogo Topliva*, **8**, 666-76 (1937).

²¹⁵ Sapozhnikov, L. M., and Cherkasskaya, E. I., *ibid.*, **6**, 28-33 (1935). See also refs. 154 and 155.

²¹⁶ Bakun, N. A., *Coke and Chem. (U.S.S.R.)*, **4**, Nos. 5-6, 112-7 (1934).

²¹² Sapozhnikov, L. M., and Eidel'man, A. E., *Khim. Tverdogo Topliva*, **5**, 590-5 (1934). See also ref. 154.

²¹³ Strongin, A. S., and Taits, E. M., *Coke and Chem. (U.S.S.R.)*, **4**, No. 12, 16-24 (1934). Er-

times, as abscissas. The experimental points were joined by smooth curves. In the example given the yield of gas on the hot side was only slightly larger than that on the cold side up to 590° C; thereafter, that on the hot side increased rapidly for about 75 minutes. For this particular coal the total yield of gas from the cold side was 1.7 liters, or 19.54 percent of the total yield from both sides. Apparently, thickness of the plastic layer was measured separately in the apparatus used in the usual plastometric investigation, inasmuch as no provision seems to have been made for taking these measurements in the special apparatus described for determining volumetric gas yields from the hot and cold sides of the coal charge.

In general, for the 28 coals studied, those with the same thickness of plastic layer gave nearly the same percentage yield of gas on the cold side, independent of the extent of aftershrinkage of their semicokes. Thus, 2 coals with almost the same thickness of plastic layer, 12 and 13 millimeters, gave gas yields of 29 and 28 percent by volume, respectively; their "settlings," however, differed greatly—10 and 27 millimeters, respectively. Seven coals with plastic layer thicknesses ranging from 18 to 23 millimeters showed gas yields between 14.3 and 17 percent, and settlings between 8 and 25 millimeters. Four coals with plastic layer thickness ranging from 30 to 34 millimeters gave gas yields between 8.2 and 10.5 percent, and settlings from 2 to 11 millimeters. Data for the other 15 coals were not plotted, but a study of the tabulated data shows the same general trends although more irregularities than in the 13 coals selected for plotting.

One may make the general conclusion that, as the plastic layer increases in thickness, the percentage by volume yield of gas on the cold side decreases. This relation-

ship is independent of the aftershrinkage of the semicoke. A plot showing thicknesses of the plastic layer, in millimeters, as abscissas versus percentage by volume of gas yield on the cold side as ordinates gave a fairly smooth logarithmic type of curve for the 28 U.S.S.R. coals tested. For the 10-millimeter difference in plastic layer between 30 and 20 millimeters the gas yield increased 6.5 percent (from 10 to 16.5 percent), but for the same difference between 20 and 10 millimeters the yield increased 16 percent (from 16.5 to 32.5 percent). When the thickness of the plastic layer was 5 millimeters, the gas yield rose 29.5 percent (from 32.5 to 62 percent). For coals with plastic layer thicknesses of 5, 10, 15, 20, 25, 30, and 35 millimeters¹⁵⁴ the corresponding gas volume yields on the cold side were 70, 35, 22, 16, 12, 10, and 9 percent. Thus, as the thickness of the plastic layer increased, the volume yield of gas on the cold side decreased rapidly.

Bakun,²¹⁶ in the earlier study, showed that as the degree of oxidation of a coal was increased the quantity of gas given off on the cold side increased, and that on the hot decreased correspondingly. This meant that, on oxidation, the plastic mass became less homogeneous and, consequently, more permeable to the passage of gas.

Pashkevich²¹⁷ found that coals producing a considerable plastic layer and small contraction during coking showed a decrease in rate of gas evolution during the plastic range and a corresponding increase during the period following the plastic range as the rate of heating was increased; the maximum of the gas-evolution curve was displaced toward the higher temperature. With coals giving a thin plastic layer and high contraction there was no displacement of the maximum of the gas-evolution

²¹⁷ Pashkevich, A. Z., *Coke and Chem. (U.S.S.R.)*, 6, No. 9, 27-32 (1936).

curve with increase in rate of heating. The rate of gas evolution increased regularly during both the above-named stages of coking as the rate of heating was increased.

Fluidity of the Plastic Layer. Sapozhnikov and Finkelstein^{153, 154, 155} determined the rate of flow and temperature of the plastic layer of coal during its extrusion through a 5-millimeter orifice. The size of the coal charge, the rate of heating, and the external pressure applied to the coal charge were the same as in the plastometric investigation, but the retort of the apparatus was provided with two side-wall openings. The orifice for the extrusion of the coal was a round hole, 5 millimeters in diameter, drilled through the side wall of the retort at a distance of 10 millimeters above the upper surface of the retort bottom. This hole was kept tightly closed by an adjustable iron plug until the plastic coal had reached this level during the test. Diametrically opposite to this orifice and on the same level was a second hole, through which was inserted a thin, tightly fitting thermocouple to measure the temperature of the plastic mass of coal during its extrusion through the orifice.

Sapozhnikov¹⁵⁵ stated: "The coal is heated at 3° C per minute. . . . At the start, the experiment is exactly the same as the usual plastometric test until the solidified coke layer reaches 8 millimeters in thickness 112 minutes from the beginning of the experiment. Then the plug which closes the hole is taken out and the plastic mass is allowed to flow out the hole." It would appear that Sapozhnikov must have meant that this thickness of coke layer and time applied only to his illustrative example of the test, because these definite values would not necessarily be the same for other coals. Furthermore, his "beginning of the experiment" in his illustrative plot of the results indicated a

temperature of 270° C, and "112 minutes from the beginning of the experiment" indicated a temperature of about 595° C, which would seem too high for coal to remain plastic. The abscissas of the diagram indicated that the time interval from 10 to 130 minutes corresponded to the temperature range from 290 to 635° C. This would mean an average heating rate of 2.875° C per minute. However, the plotted data showed that the 10-minute scale divisions of time corresponded to temperature intervals varying from 25 to 40° C, and heating rates from 2.5 to 4.0° C per minute. Sapozhnikov¹⁵⁵ further described the observations made in the test:

The gases which have accumulated in the plastic layer escape first through the hole; this is accompanied by an abrupt drop of the lever. Then at 112 minutes the plastic mass appears, being squeezed out of the hole in the form of a rod of the same diameter as the hole from which it flows. This plastic rod swells under the inner pressure of the decomposition gases and quickly expands to 8 or 10 millimeters for coals of lower plasticity, and up to 35 or 40 millimeters for highly plastic coals. This rod is received in a grooved spout and towards the end of the experiment it attains a considerable length. After an abrupt drop the volume curve becomes rectilinear; the thickness of the plastic layer decreases quickly, and the coke layer stops growing. The slope of this straight line gives the velocity of outflow. The fluidity is represented by the tangent of the angle α . To simplify calculations, instead of the tangent we took as index of fluidity the vertical component BC in millimeters with a constant time base AC corresponding to 5 minutes.

[This angle α is formed by the straight-line portion of the volume curve and a base line drawn parallel to its "zero" or datum line. The constant time base AC , read from Sapozhnikov's chart, appears to correspond to 10 minutes. If 10 is correct then the vertical component BC is twice that when

the constant time base is 5. The relative indexes of fluidity for different coals would remain in the same order in either case.] Sapozhnikov found that, if the outlet was opened several times during the experiment, no material flowed out when the upper or middle part of the plastic layer was opposite the orifice; only the very lowest part was able to flow out. After the test, the coke column, therefore, had a horizontal upper surface without any signs of slope toward the orifice in the wall of the retort.

Test results on 20 U.S.S.R. coals were plotted in a plastometric diagram. The abscissas represented the final drops of the expansion-pressure curve in millimeters and the ordinates the maximum thicknesses of the plastic layer in millimeters. Each plotted point representing a coal on the diagram was marked further by a numeral defining its fluidity index value, or, for non-fluid coals, by an X.

The 20 coals divided themselves into four general groups. The 8 nonfluid coals formed very viscous plastic layers between 5 and 21 millimeters in thickness and showed final drops in their expansion-pressure curves between 7 and 45 millimeters. A straight line inclined to the left across the classification diagram (such as line *op* in Fig. 11) separated 7 of these nonfluid coals into the lower part of the diagram. The upper right part of the diagram above the inclined line included 5 coals with "fluidity index" values between 2 and 14, thicknesses of plastic layer between 20 and 34 millimeters, and final drops in their expansion-pressure curves between 0 and 10 millimeters. Five coals in the middle of the diagram above the inclined line had fluidity indexes between 13 and 17, thicknesses of plastic layer between 19 and 30 millimeters, and final drops in their expansion-pressure curves between 17 and 21 millimeters. The fluidity indexes increased

markedly with increase in thickness of the plastic layer. Two coals in the upper left part of the diagram showed fluidity indexes of 20 and 22 with corresponding thicknesses of plastic layer of 16 and 23 millimeters, and final drops in their expansion-pressure curves of 31 and 34 millimeters, respectively. In general, therefore, for a series of coals that develop fluidity it may be concluded (1) that the fluidity increases with increase in thickness of the plastic layer, and (2) that the coals in the upper left part of the diagram become more fluid than those in the upper right part.

The effect of increasing the rate of heating from 5 to 7° C per minute was to increase fluidity-index values.

The influence of the degree of pulverization of the coal charge on its fluidity index was studied.¹⁵⁵ Under like conditions of coking, a given coal should produce the same total quantity of liquid from large or small particles, but when this liquid is fused out on their surfaces the smaller particles, because of their greater total surface area, will be coated with a thinner film of liquid. Coals that are quite fluid when coarsely pulverized, therefore, should have less or no fluidity when ground finely enough.

To test this hypothesis, Sapozhnikov plotted the fluidity index against the degree of pulverization of a coal. This coal (from the left part of classification diagram) had a plastic layer thickness of 18 millimeters and a final drop in the expansion-pressure curve of 29 millimeters. The original fluidity index of about 14 was retained as the size of coal particles was reduced from 2 to 0.9 millimeter, and then dropped gradually to zero for particles of 0.05 millimeter. Similar tests on a coal (from the right part of the classification diagram) with a plastic layer thickness of 32 millimeters and a final drop in the expansion-pressure curve of 10 millimeters

showed an increase in fluidity index from 15 to 17. Sapozhnikov¹⁵⁵ stated that "grains of coals of this kind soften uniformly, and the smaller the diameter of the grains the more quickly the limit to which they may be softened is reached." The middle part of the diagram represents coals with intermediate properties.

To summarize, then, in going from left to right across the classification diagram, the liquid fused out onto the surface becomes more and more viscous, and the remainder of the coal-grain mass becomes softer and softer until, in the right part of the diagram, the difference between coal grains disappears entirely.

Gas Permeability of the Plastic Layer.

Sapozhnikov and Cherkasskaya^{154, 155, 200} determined the gas permeability of the plastic layer of coal from measurements of the pressure that had to be applied to permit penetration of gases through the plastic layer from the hot to the cold side of the heated charge. Under the test conditions a coal, depending on its type, developed no pressure at all or a pressure under 1 atmosphere or else it developed *at once* a pressure of 50 atmospheres or more. The division between the two types was marked by curve *mn* in Fig. 11; coals lying below this curve showed pressures of less than 1 atmosphere; those lying above, 50 atmospheres or more. There were almost no transitional coals having gas-pressure permeability values intermediate between these two. It was observed for the 44 Donets coals tested that coals of the first type had thin plastic layers (13 to 16 millimeters) and final drops in their expansion-pressure curves up to 30 millimeters, whereas coals of the second type had thicker plastic layers and final drops generally not greater than 22 millimeters.

Mechanism of Coking. Sapozhnikov¹⁵⁵ drew certain conclusions regarding the

mechanism of coking of U.S.S.R. coals from data obtained by the plastometric investigation and its modifications for the study of special properties of the plastic layer of coal. These conclusions may be summarized conveniently from the composite diagram, Fig. 11.

Coals in the lower right part of the diagram (below curve *mn*) developed a high expansion pressure, of the order of 0.5 to 0.6 kilogram per square centimeter. They did not, however, offer any appreciable resistance to the passage of gas. The expansion pressure was due to gases accumulated inside the coal grains themselves, which had so little mobility and were so slightly adhesive that they did not stick together in a continuous film under high pressure (0.5 kilogram per square centimeter) acting from inside the individual grains. Gases liberated on the hot side of the plastic layer could pass unhindered between the coal grains.

For coals above curve *mn* a sharp drop occurred in the gas permeability of the plastic layer. The increased mobility of the plastic grain mass caused the formation of a gas-proof plastic layer, which, however, remained quite viscous. For coals between curves *mn* and line *op* the thickness of the plastic layer continued to increase, but the coals did not become fluid until their coordinates lay above line *op*. The fluidity of the plastic layer of the coals in the upper right part of the diagram increased slowly as the thickness of the layer itself increased. This thickness finally reached a high value, around 35 millimeters. Coals in this part of the diagram (thickness of plastic layer, above 20 millimeters; and coke shrinkage, 0 to 10 millimeters) were coked by the softened grains growing together in the plastic period along their contact surfaces, while neighboring grains were pressed into one

another by gaseous decomposition products that accumulated inside them.

The coals in the lower left part of the diagram behaved entirely differently; they did not give an expansion pressure, they were not fluid, and their plastic layers did not offer any resistance to the passage of gases. The grains of these coals, therefore, could not hold the gases liberated inside them. As the plastic layer increased, no expansion pressure was developed, and the plastic layer remained permeable to gases until it reached 10 to 15 millimeters in thickness. Fluidity then suddenly appeared in the plastic mass and attained a high value, but the plastic layer increased for another 5 to 6 millimeters before it became impermeable to the passage of gases. Sapozhnikov¹⁵⁵ stated that it was assumed that

the liquid bituminous constituent of the grains of these coals is fused out on to the surface of the grains. While the plastic layer is small [thin], and there is little liquid, the system is not fluid and gases pass through it unhindered. The insufficient quantity of liquid is distributed on the surfaces of the grains in the form of very thin films, which stick the grains together and limit their mobility. As the quantity of liquid increases, the films become thicker and there finally comes a time when it is possible for the solid particles to slide over one another and the system immediately almost reaches its limit of fluidity, the subsequent fluidity increase being small. However, it does not become gas proof until the liquid fills up all the spaces between the particles; liquid is then present in considerably greater quantity than is necessary for fluidity to appear. This kind of coal is apparently coked mainly by the coal particles being cemented by the decomposition products of the liquid phase.

Experience in the U. S. Bureau of Mines laboratories with plastometric investigation for measuring the thickness of the plastic layer of coal has been disappointing. One

difficulty arises from the lack of a more suitable criterion than the "feel" method to assure oneself that the tip of the measuring needle is actually at the desired height of measurement, especially when determining the *top* level of the plastic layer. Another difficulty is the long time lag before the thermocouple attains a steady reading at a given height in the charge. These obstacles may actually have been overcome by the Russian investigators. The difficulties in transliteration of the characters of the Russian alphabet and in the translation of the published papers into more widely read languages have handicapped workers outside of the U.S.S.R. in evaluating Russian scientific work. Nevertheless, the plastometric investigation appears basically sound, and the wide application of this method in conjunction with modifications of its general principle for measuring special properties of the plastic layer to provide supplementary information would indicate future usefulness in the classification and evaluation of U.S.S.R. coals.

The writer is deeply indebted to H. G. Landau, member of the staff of the Coal Research Laboratory at the Carnegie Institute of Technology, for translations of several and for invaluable aid in interpretations of a number of other Russian publications that have been reviewed.

PLASTICITY AND SWELLING OF COAL DURING COMBUSTION

Within recent years there has been a growing interest in measurements of the plastic and swelling properties of coals as they develop under different conditions of combustion. Satisfactory methods for obtaining quantitative measurements directly have not yet been devised. Most of the methods so far developed stipulate the use of finely ground coal, a definite rate of heating out of contact with air, and appa-

ratus of limited size. These conditions are precisely the opposite of those desired for the most favorable combustion of coal on industrial grates.

Sherman and Kaiser²¹⁸ have made diagrammatic sections (a) of actual fuel beds of different bituminous coals based upon direct observations during the course of burning tests in a small underfeed stoker, and (b) of the carefully disassembled beds left after these tests. For a relatively free-burning bituminous coal the plastic zone was shown to begin at about the level of the lower row of tuyères in the stoker and to increase in thickness toward the center of the retort. The plastic zone near the tuyères was thin because of oxidation by air. It was thicker in the center because of less penetration of air and the longer time for development of plasticity and cementation of particles. With a more strongly caking coal the plastic zone was somewhat higher in the retort and was considerably thicker than with a more freely burning coal.

The time during which the coal is plastic and its degree of fluidity determine the distance the material can flow under the pressure to which it is subjected. Hence, for a given coal the sizes of particles and voids determine the degree of cementation of the particles. In underfeed-stoker operation the fines tend to concentrate at the back of the retort and the coarse coal at the front. It is doubtful that the common practice of removing fines from stoker coal, either to reduce coke-tree formation, to reduce the ash content, or to render the coal less dusty, is economically desirable or technically necessary. Sherman and Kaiser concluded that proper adjustment of the

size range generally will reduce or eliminate these difficulties in most coals.

Dunningham and Grumell^{219, 220} determined the swelling properties of coal during combustion, under conditions of a traveling-grate fuel bed. Their apparatus²¹⁹ consisted essentially of a mild-steel pot, 12 inches in diameter and 12 inches in height. Its perforated bottom plate was covered by a 3-inch bed of graded silica, which served as a grate. By careful distribution of the coal in layers, a 3- or 6-inch bed of coal of uniform density was built up on this grate. The bed of coal was ignited on the top surface, and air was passed upward at a controlled rate through the fuel bed; ignition continued downward until the ignition plane reached the grate. Comparison of the total depth of fuel bed at the end of the ignition period with the original depth gave the extent of swelling (or contraction). Measurements were accurate to within 0.5 inch.

In the earlier study²¹⁹ the authors showed that the resistance of fuel beds of free-burning and coking coals was highest before the coal was ignited and was then gradually reduced as the ignition plane progressed downward, there being a marked drop as soon as the ignition plane reached the grate. With slightly coking coals, the resistance of the fuel bed increased to a maximum until the plane of ignition reached the grate and then, as with the other coals, it dropped suddenly. Further experiments²²⁰ showed that this difference in behavior could be effected by change in size of the coal. Tests on coal mixtures in a 6-inch bed at an air rate of 190 pounds per square foot per hour showed that with decrease in the graded sizes both initial re-

²¹⁸ Sherman, R. A., and Kaiser, E. R., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 388-407 (1938).

²¹⁹ Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel*, **9**, 24-9 (1935).

²²⁰ Dunningham, A. C., and Grumell, E. S., *Fuel*, **17**, 324-7 (1938).

sistance and thickness of the fuel bed increased. However, when the ignition plane reached the grate, the resistance increased to a maximum for sizes above $\frac{1}{4}$ inch, whereas this resistance for coal under $\frac{1}{4}$ inch decreased from the initial value. Although the larger sizes began with a lower initial resistance, this resistance increased, whereas the smaller sizes began with a higher initial resistance, which decreased. It is probable that during the ignition period the average resistance for the two sizes would be much the same.

The effects of ash content, rate of air flow, size of coal, and depth of fuel bed were studied²²⁰ for a free-burning, High Hazel Seam, Derbyshire County, coal, and for 2 coking coals, Parkgate and Silkstone Seams, both from Yorks County, England. A series of fuel beds of varied ash content was prepared from each coal by mixing proper proportions of the float (1.35 sp. r.) and sink (1.60 sp. gr.) portions. Air rates of 110, 190, 290, and 355 pounds per square foot per hour, equivalent to combustion rates of 15, 25, 37, and 49 pounds per square foot per hour, were used.

All samples of free-burning High Hazel Seam coal (ash contents, 2.3 to 16.7 percent) at the air rate of 110 pounds per square foot per hour, and also those with ash contents up to 8.2 percent at the air rate of 190, showed swelling for both the 6- and 3-inch beds. The extent of swelling was least in the samples of highest ash content. Samples with more than 8.2 percent ash at the air rate of 190 pounds per square foot per hour and all samples at air rates of 290 and 355 showed shrinkages. For all air rates, almost linear reduction in the fuel-bed level occurred as the air rate increased, independent of the ash content.

All the Parkgate Seam samples (ash contents, 2.9 to 15.7 percent) showed swelling except those of ash content above 8.6 per-

cent and at the highest air rate of 355 pounds per square foot per hour. Swellings of 10 to 13 inches of the 6-inch fuel bed were observed. With the 3-inch beds the effect of the ash was less pronounced. Small reductions in fuel-bed level occurred at air rates of 110 and 190, rather more at 290, and finally a large but gradual reduction at the air rate of 355 pounds per square foot per hour.

One may conclude that there was an undoubted tendency throughout for increasing ash content to reduce swelling, which for highly swelling coking coals might become very pronounced. It appeared that for strongly coking coals at high rates of air supply the effect might depend to some extent on the original thickness of the fuel bed. The difference between free-burning and coking coals was quite pronounced. When the ignition plane had reached the grate, the thickness of the fuel bed of coking coals, at all but the lowest air rates, was two to three times that of the free-burning coal, even when the high ash content and high air rate had reduced the tendency to coke.

The effect of graded sizes of High Hazel Seam coal, the Parkgate Seam coal, and a mixed sample of the two upon the swelling of their 6-inch fuel beds was studied. Each sample contained 3 percent ash and was tested at an air rate of 190 pounds per square foot per hour. With the free-burning, High Hazel Seam, coal the slack plus 5 percent of water swelled no more than the sizes graded above $\frac{1}{2}$ inch. With Parkgate Seam coal and the mixture, the slacks gave intermediate values. Comparisons were made of the swelling of "graded $\frac{1}{4}$ to $\frac{1}{2}$ inch" and "slack plus 5 percent water" samples of Silkstone Seam coal containing 3 and 12.3 percent ash in 6-inch fuel beds and at air rates of 110, 190, 290, and 355 pounds per square foot per

hour. The samples containing 3 percent ash showed the same swelling in both sizes, but in the samples containing 12.3 percent ash the sized $\frac{1}{4}$ - to $\frac{1}{2}$ -inch coal swelled slightly more than the slack samples at the higher rates of air supply.

The investigations of Dunningham and Grumell indicated that, by suitable adjustment of ash content, air rate, size of coal, and fuel-bed thickness, coals with more than 83 percent carbon, considered unsuitable for gas producers and small automatic stokers, might be usable. Coals containing about this percentage of carbon (High Hazel Seam, 81.35; Parkgate Seam, 85.28; and Silkstone Seam, 86.49 percent) differ in practical performance out of all proportion to small changes in rank. Further work of this nature should prove of advantage in extending the range of coals available for the two purposes mentioned.

PLASTICITY AND COAL SELECTION

The application of plasticity data to the selection of coals for various purposes has been discussed by Brewer.²²¹ The discussion referred to certain items in the Coal Selection Charts published in 1936 by the National Committee on Coal of the National Association of Purchasing Agents. The plastic properties of coals of different rank and type were classified upon the basis of their behavior in the Davis plastometer test⁹⁰ into five general divisions. The importance of plasticity with reference to the uses of such coals in various types of combustion installations, for gas- and coke-making, metallurgical practice, domestic stokers, and briquetting, was emphasized. For further details the two papers should be consulted in conjunction. Ben-

ton²²² has found that coals showing a short plastic temperature range and low maximum resistance in the Davis plastometer test behave well in the domestic stoker.

COMPARISON OF RESULTS OF TESTS OF PLASTIC PROPERTIES DETERMINED BY DIFFERENT METHODS

In many of the investigations reviewed in the foregoing sections of this chapter, determinations of the plastic and related properties of bituminous coals have been made by more than one method. Frequently, however, the published descriptions of the work have been too meager to permit evaluation of the worth of individual methods as used by a given investigator. It is recognized that the many variables in test sample, apparatus, and procedure were not always controlled. A few laboratories, however, have carried out determinations by different methods under conditions that permit comparison of the results obtained. Among others, the investigations of Gieseler, Curtis and coworkers, and the U. S. Bureau of Mines workers illustrate the agreement that may be expected among the different methods.

Results of tests on 9 Ruhr, 5 Lower Silesian, and 6 Upper Silesian German coals obtained by Gieseler using the penetrometer, Foxwell gas-flow, and plastometer test methods^{24, 110} are summarized in Table IV. The remarkable agreement of the temperature limits for the "softening zone" obtained by the penetrometer and plastometer tests is somewhat surprising in view of the fact that coal samples for the plastometer investigation¹¹⁰ had been stored for more than a year and "thereby the Silesian coals, especially, had lost in caking capacity." The softening points by

²²¹ Brewer, R. E., Natl. Assoc. Purchasing Agents, Article 20, Jan. 13, 1938, 7 pp. (mimeographed).

²²² Benton, E. D., *Coal-Heat, The Stoker Magazine*, 38, No. 5, 5-8, 44-5, No. 6, 5-10 (1940).

TABLE IV

COMPARISON OF PLASTICITY DATA OF GIESELER

Coal	Volatile Matter, Pure Coal	Softening Zone		Foxwell Test		Modified Penetrometer Test			Plastometer	
		Penetrometer	Plastometer	Softening Point	Resolidification Point	Swelling Range		Swelling	Zone of Greatest Plasticity	Highest Value of Plasticity
						Begins	Ends			
Ruhr	percent	°C	°C	°C	°C	°C	°C	percent	°C	angular degrees
A	17.3	463-515	461-515	474	537	468	501	19	482-490	1
B	18.2	410-503	413-503	440	530	431	485	74	455-480	13
C	20.7	405-512	402-512	405	527	425	487	97	433-483	63
D	22.1	380-502	376-493	400	481	391	463	115	407-472	115
E	23.3	386-506	380-500	407	473	400	471	146	410-475	120
F	24.3	388-502	400	470	397	466	137
G	25.3	390-510	402	511	405	467	150
H	25.4	384-506	401	471	398	466	226
I	26.0	374-502	373-497	385	472	398	461	260	403-476	c. 200
Lower Silesian										
K	24.7	395-504	390-503	398	508	406	464	18	426-450	14
L	26.9	398-491	405	494	401	459	15
M	28.2	389-505	384-495	400	493	398	461	75	423-457	19
V	32.6	377-461	375-462	412-444	39
N	34.8	370-477	367-475	390	464	401	425	12	313-439	21
Upper Silesian										
O	29.6	373-497	370-490	393	457	391	461	137	403-468	c. 600
P	32.5	375-495	372-483	400	453	393	452	76	413-457	63
R	34.7	382-472	398	479	400	446	13
S	35.7	378-498	378-468	400	486	398	430	11	414-440	29
T	36.2	381-469	379-468	400	467	413	413	20	424-431	7
U	36.3	388-456	400	440	404	422	6

the Foxwell test are seen to be generally higher than those for the beginning of the "softening zone" as determined by the other two methods. On the other hand, the resolidification points are higher than, the same as, or lower than the end temperatures of the softening zone. Such variations, however, have often been observed between data by the Foxwell gas-flow test and other methods.

With decrease in rank of the Ruhr coals, the percentage of swelling and the highest value of plasticity increased quite regularly. This regularity was not observed with the Silesian coals. The general tend-

ency here, especially for Upper Silesian coals, was for the swelling and plasticity values to decrease with decreased rank (increased volatile matter) of the coals. The general trend for the plasticity (more correctly, fluidity) of bituminous coals to increase with decreasing rank of the coal up to a maximum value and then decrease has been observed also by other workers.^{142, 65, 91} Peak values for fluidity depended not only on rank but also on petrographic composition of the coals tested.

Investigations with the modified heating microscope of Leitz, using coals of grain size between 0.25 and 0.4 millimeter,

showed²⁴ that the Ruhr forging coal *A* (see Table IV) remained unchanged up to 470° C; all grains then softened between 495 and 500° C and immediately solidified again. The Ruhr coking coal *I*, on the other hand, softened between 375 and 410° C and remained plastic to 500° C. Lower Silesian coking coal *K* showed the first change at 402° C. Complete softening took place between 420 and 450° C, and expansion occurred up to 500° C. Upper Silesian coal *O* first changed shape at 390° C, at which temperature the edges of the grains rounded off, and then softened at 400° C. The coal remained plastic for a long time and swelled to a large cone. Upper Silesian gas flame coal *U*, on the other hand, showed only partial fusion at 405° C. The top surfaces and shapes of the coal grains remained practically unchanged.

Ball and Curtis¹⁸ found good agreement between the softening temperatures of individual particles of coal observed in a microfusion apparatus and of a column of particles of the same coal determined by a modified Foxwell gas-flow test. Results for 9 coals are shown in the first four columns of Table V. The last four columns of this table give data obtained by Lum and Curtis¹³⁷ with their extrusion test methods on 6 coals of similar rank.

Malleis²²³ summarized and discussed the practical significance of the plastic properties of 32 American coals and 14 blends tested by the U. S. Bureau of Mines by the Layng-Hathorne gas-flow, Agde-Damm dilatometer, and Davis plastometer test methods as originally developed⁸⁸ or with

²²³ Malleis, O. O., *Proc. Am. Soc. Testing Materials*, **37**, Pt. II, 402-20 (1937).

TABLE V

COMPARISON OF SOFTENING TEMPERATURES BY MICROFUSION AND GAS-FLOW TESTS
AND EXTRUSION DATA ON SIMILAR COALS (Curtis and coworkers)

Coal Seam	Volatile Matter, Dry Basis	Micro-fusion Test	Gas-Flow Test	Coal Seam	Volatile Matter, Dry Basis	Extrusion Tests	
		Distortion Temperature	Softening Point			Initial Temperature of Maximum Extrusion	Average Extrusion
	percent	°C	°C		percent	°C	grams per minute
Big Vein (Pittsburgh)	15.0	430	440				
Fulton	15.9	440	440				
Kittanning	16.3	430	435				
Moshannon or Lower Freeport	17.1	425	430	B or Lower Kittanning	17.5	500	1.15 *
Beckley	17.3	425	430	Lower Kittanning	22.3	440	0.24 †
Pool 71	23.1	395	395	Imboden	34.0	420	0.48 †
Moshannon	23.8	395	410	Pittsburgh	34.8	420	1.17 †
Winifrede	38.1	380	380	No. 2 Gas	36.1	430	1.59 ‡
Black Creek	38.3	385	400	Deepwater Black Creek	39.1	Not plastic enough	

* Uncorrected data obtained with 0.795-centimeter-diameter orifice.

† With 0.397-centimeter-diameter orifice.

‡ With 0.238-centimeter-diameter orifice.

later improvements.⁹⁰ The significance of the measured plastic properties in connection with coke manufacture and combustion was emphasized. Insufficient data at that time on low-volatile coals precluded generalizations, but results on high-volatile coals permitted general predictions of the quality of cokes to be expected and of the com-

A comparison of characteristic plasticity data obtained by the Davis and Gieseler plastometer methods and expansion data determined by the sole-heated and slot test ovens by the U. S. Bureau of Mines is given in Table VI. With decreasing rank of the coals, fusion and fluidity temperatures decrease. Maximum fluidity of the

TABLE VI
COMPARISON OF PLASTICITY AND EXPANSION DATA (U. S. BUREAU OF MINES)

Coal Seam	Dry Mineral-Matter-Free Volatile Matter	Fusion Temperatures by Plastometer Tests		Gieseler Maximum Fluidity, Maximum Pointer Movement		Davis Blastometer Maximum Resistance	Expansion at Bulk Density of 55.5 Pounds per Cubic Foot	
		Gieseler	Davis				Sole Oven	Slot Oven
	percent	°C	°C	°C	div./min	lb-in.	percent	percent
Pocahontas No. 4	18.0	...	473	479	3	111	+22.6	+27.8
Pocahontas No. 3	18.4	463	460	476	18	107	+17.8	+19.9
Sewell	22.5	435	433	461	89	38	+11.7	+16.8
Lower Banner	23.1	430	424	467	290	28	- 6.2
Pond Creek	33.9	405	410	429	1,250	18.5	- 6.6	- 7.6
High Splint	40.1	394	410	426	6	9.5	- 8.6	- 9.3

bustion characteristics of such coals when burned in stokers.

Publications by different workers in U. S. Bureau of Mines laboratories^{87, 88, 89, 90, 91} have given comparisons of data obtained on the same coals using Layng-Hathorne gas-flow, Agde-Damm dilatometer, Davis plastometer, and Gieseler plastometer methods. The publications cited and a paper²²⁴ listing twenty-two other publications show the order of agreement of data obtained by these methods on about 100 coals and blends and the usefulness of these data in predicting the gas-, coke-, and byproduct-making properties of American coals.

²²⁴ Fieldner, A. C., Davis, J. D., Reynolds, D. A., Brewer, R. E., Sprunk, G. C., and Schmidt, L. D., *U. S. Bur. Mines, Tech. Paper 616* (1940), 47 pp.

coals increases with rank and then decreases. The Davis plastometer maximum resistance values decrease regularly, as do the expansions determined in both types of test ovens. These data are characteristic generally for coals of the ranks indicated. Upon the basis of rank alone, the decided change from expansion to contraction in going from Sewell to Lower Banner coal would not appear plausible. However, these two coals differed markedly in petrographic composition. The Sewell coal contained 81 percent (by area) bright, 15 percent semisplint, and 4 percent splint coal, whereas the Lower Banner consisted of 36 percent bright, 53 percent semisplint, and 11 percent cannel coal. One would, therefore, expect the Sewell bed coal to expand and the Lower Banner bed coal to contract.

TABLE VII

CLASSIFICATION OF COALS ACCORDING TO DANGEROUS OR SAFE EXPANDING PROPERTIES BY
THREE TESTS (All bulk densities on dry basis)

Coal Designation	Volatile Matter, Parr Basis	Bulk Density, 750 kg per cu m			Estimated Lowest Dangerous Bulk Density	
		Old Standard, Test 1	Ordinary Firebrick, Modified Test 2	Insulating Firebrick, Modified Test 3	Test 2	Test 3
Durham	percent					
7 B.P. Brockwell	26.0	Safe	Safe	Safe		
17 T.L. Victoria	26.5	Safe		
16 B.P. Victoria	26.8	p.d.	Safe		850
4 L	27.2	d.	Safe		
6 T	27.4	p.d.	Safe		
3 D	27.6	p.d.	Safe		
2 F	28.6	d.	Safe		
1 B	29.2	p.d.	Safe	Safe		
13 D.L. Brockwell	31.5	Safe	Safe		
11 S	31.7	Safe	Safe	Safe		
5 C	32.8	Safe	Safe		
12 E.H.	33.3	Safe	Safe		
10 K	33.4	Safe	Safe	Safe		
15 D.L. Busty	34.9	Safe	Safe		
8 Betco	35.5	Safe	Safe		
9 Veco	36.2	Safe	Safe		
14 D.L. Harvey	37.0	Safe	Safe		
South Wales						
12 Anthracite Stanlyd	5.8	p.d.	d.	Safe		
10 N. lower 5 ft	16.0	Safe	Safe	Safe		850
1 P.A.	17.3	Safe	Safe	Safe		825
9 N. upper 5 ft	19.6	Safe	Safe	Safe		825
11 N. new	21.9	Safe	Safe	Safe		825
6 G.N.T.	22.1	Safe	Safe	Safe	775	775
8 N. 2 ft 9 in	22.5	Safe	Safe	Safe		800
7 G.N.	24.7	Safe	d.	d.		725
3 P.C.	25.4	Safe	Safe	Safe		850
2 P.B.	25.5	v.d.	d.	d.	750	700
4 G.L.	27.4	Safe	Safe	Safe	875	900
5 G.B.	29.8	p.d.	Safe	Safe	925	900
Somerset						
1 W.D. b	29.8	d.		
1 W.D. a	30.1	p.d.	d.	d.		800
Kent						
1 Beresford 3 ft	25.5	p.d.	d.	Safe	775	800
South Yorkshire						
1 Silkstone	Safe		
2 Parkgate and Silks	34.6	Safe	Safe		
German						
1 O.	20.0	p.d.	d.	d.		650
2 E.F.	22.6	v.d.	d.	d.	650	725
3 K.L.	27.3	Safe	d.	Safe		825
American						
1 Kittanning	17.2	p.d.	d.	d.	600	625
3 Pocahontas	18.2	Safe	d.	d.	650	750
2 Sewell	22.4	Safe	Safe	Safe	800	775
Canadian						
Michel	27.2	Safe	Safe	Safe	825	850

COMPARISON OF EXPANSION PRESSURE TEST METHODS AND RESULTS

Any prediction, based upon measurements made in small-scale laboratory tests or even in small experimental test ovens, of the safe, possibly dangerous, or dangerous expansion pressure to be expected to be developed by a given coal when coked under conditions of commercial coke-oven practice is likely to prove misleading. Fortunately, the test results almost always indicate a higher expansion pressure than appears to be developed by the coal in the

coke oven, thus providing a factor of safety.

Comparative test results obtained by one or more methods on 42 representative English, German, and American coking coals have been published by Mott and Spooner.^{161, 165} The safe, or relatively dangerous, expanding properties of these coals are classified in Tables VII and VIII.

The classifications safe, possibly dangerous (p.d.), dangerous (d.), and very dangerous (v.d.) were based on the following summarized conditions for each of the seven test methods.

TABLE VIII

CLASSIFICATION OF COALS ACCORDING TO DANGEROUS OR SAFE EXPANSION PROPERTIES
BY FIVE TEST METHODS

Coal Designation	Baum-Heuser Test at Dry Bulk Density of 750 (or 800) kg per cu m	Koppers Large-Scale Swelling Test (Charge Wrapped in Asbestos Paper) at Dry Bulk Densities of 750 800 850 kg per cu m			U. S. Bureau of Mines, Slot and Sole-Heated Ovens as Tested at Bulk Density of 830 kg per cu m 870 kg per cu m	
		Nedelmann Test at Dry Bulk Density of				
Durham						
16 B.P. Victoria	Safe	Safe	Safe *	d.		
1 B.	Safe	..	d.	..	d.	
South Wales						
7 G.N.	d.	d.	d.	..	d.	
2 P.B.	d.	d.	d.	..	d.	
Somerset						
1 W.D. a	d.	Safe	Safe *	..	d.	
Kent						
1 Beresford 3 ft	Safe	..	Safe	..	d.	
German						
1 O.	d.	d.	d.	..	d.	
2 E.F.	d.				d.	
American						
1 Kittanning	d.				d.	Particularly dan- gerous
3 Pocahontas	d.				d.	Dangerous
2 Sewell	Safe					Dangerous
Yorkshire T.P.		d.†	d.			

* Safe with minus ½-inch coal.

† Dangerous when not wrapped with asbestos.

A. *Koppers A.-G. "Laboratory Method"* (Koppers Small-Scale Swelling Test or Old Standard Test). Based upon movement of indicator in millimeters from zero datum line (3.6 times that of charge, 3.0 more usual; pressure 1.16 kilograms per square centimeter, 1.0 or 1.165 kilograms per square centimeter sometimes given); bulk density, 750 kilograms per cubic meter (46.8 pounds per cubic foot, dry basis).

B. *Modified Test 2*. Contraction of 15 millimeters (11.1 percent) or less marks a coal as *dangerous* when tested at 750 kilograms per cubic meter bulk density, dry basis.

C. *Modified Test 3*. Contraction of 8 millimeters (6 percent) or less, and over 1 percent swelling marks a coal as *dangerous* when tested at 750 kilograms per cubic meter bulk density, dry basis.

D. *Baum-Heuser Test*. Based on maximum swelling pressure, classification by Otto & Co., G. m. b. H., at Bochum, and by the Verein für Überwachung der Kraftswirtschaft zur Ruhrzechen at Essen, Germany¹⁶¹ (bulk density, 800 kilograms per cubic meter, dry basis).

SWELLING PRESSURE

CLASS	kg per sq cm	CLASSIFICATION	HOW USED
1	0 to 0.5	Harmless	Can be coked without danger to oven walls.
2	0.5 to 1.0	Slightly swelling	
3	1.0 to 1.5	Average swelling	Crush finely, avoid excessive moisture, or blend with high-volatile coal.
4	Over 1.5	Strongly swelling	Blend with other (lower-swelling) coals.

E. *Koppers Large-Scale Swelling Test*. Based on maximum swelling pressure. Coal is unsafe if pressure is greater than 0.08 kilogram per square centimeter. Mott and Spooner¹⁶¹ have said, "A contraction of 3.5 percent or less marks a dangerous coal"; a slight swelling (under 1 percent) was neglected. Bulk density, 750 kilograms per cubic meter, dry basis.

F. *Nedelmann Test*. Based on maximum swelling pressure. Coal is *dangerous* if pressure exceeds 1.0 kilogram per square centimeter when tested at a bulk density of 830 kilograms per cubic meter (51.8 pounds per cubic foot), dry basis.

G. *U. S. Bureau of Mines Slot and Sole-Heated Oven Test Methods*. Based upon percentages of expansion and contraction at a standard bulk density of 55.5 pounds per

cubic foot (870 kilograms per cubic meter) as tested; tentative standards:^{181b}

1. Coals with maximum expansion over 14 percent were considered *particularly dangerous*.

2. Coals with maximum expansion between 5 and 14 percent were considered *dangerous*.

3. Coals with maximum expansion between 0 and 5 percent were considered *probably dangerous*.

4. Coals whose expansion in the plastic layer was greater than the contraction during that part of the test period have not yet been evaluated.

5. Coals whose total contraction exceeded expansion during any period of the test and with a total contraction of greater than 5 percent were considered *probably safe*.

Table VII classifies the expansion properties of 41 different coals, tested by one or more of the three named test methods, as safe, possibly dangerous (p.d.), dangerous (d.), or very dangerous (v.d.). The coals from different coal beds and countries are arranged in order of increasing volatile

matter content (Parr basis), but this order does not hold for decreasing expansion. Furthermore, the tabulated expansion characteristics for a number of the coals do not agree by the three methods, although all tests were made at the same bulk density of 750 kilograms per cubic meter (dry basis).

The lack of agreement among the three test methods, even with special modifications made in the tests for some of the coals, in assessing the safe or dangerous expanding properties of coals believed to be dangerous under certain conditions led to additional tests by other widely used test

methods. The results are summarized in Table VIII.

This survey of the six test methods studied by Mott and Spooner^{19, 205} (and their collaborators) and of the slot and sole-heated oven test methods used by the U. S. Bureau of Mines¹⁸¹ for assessing the liability of a coal to damage oven walls indicates weak features in all the types of test methods compared. Because all the tests were not made at the same bulk density, comparison of the dangerous or safe expanding characteristics of the various coals, as evaluated by the several methods, cannot be made upon a common basis. Moreover, for the test methods using a bulk density of 750 kilograms per cubic meter, some coals are indicated as safe by one method but of a varying degree of danger by another method. Furthermore, the estimated lowest bulk density at which a coal becomes dangerous (columns 6 and 7, Table VII), as determined from data ob-

tained at several different bulk densities by Modified Test 2 and Modified Test 3, does not show the same order of coals for the two methods. Neither is there any strict correlation between the volatile-matter contents, Parr basis, and the dangerous or safe expanding characteristics of the coals within the different groups.

Coals showing dangerous expanding characteristics by more than one test method are listed in Table IX according to their increased content of volatile matter. The table also shows the arrangement of decreasing danger (1, 2, etc.) of the coals tested by the several methods. Blanks in the table indicate that the corresponding coals were not tested in certain methods. The dangerous coals, indicated by *d.*, *v.d.* (very dangerous), *par. d.* (particularly dangerous), and *p.d.* (possibly dangerous), show, in general, lower volatile-matter content than the safe coals, indicated by *s.* The Somerset coals are the most glaring

TABLE IX

RELATIVE ORDERS OF DANGEROUS COALS ACCORDING TO DIFFERENT TEST METHODS AND AT VARIOUS BULK DENSITIES. *A*, OLD STANDARD TEST; *B*, MODIFIED TEST 2; *C*, MODIFIED TEST 3; *D*, BAUM-HEUSER TEST; *E*, KOPPERS LARGE-SCALE TEST; *F*, NEDELMANN TEST; and *G*, U. S. BUREAU OF MINES SLOT AND SOLE-HEATED OVEN TESTS

Coal Designation	Volatile Matter, Parr Basis percent	Bulk Densities, Dry Basis, Kilograms per Cubic Meter							
		750	750	750	750 or 800	750	800	830	870
		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>		<i>F</i>	<i>G</i>
South Wales 12	5.8	p.d. 7	d. 7, 8	s. 12
American 1	17.2	p.d. 8	d. 4	d. 1	d. 3, 4	d. 2	par. d. 1
American 3	18.2	s. 10	d. 6	d. 8	d. 1, 2	d. 7	d. 2
German 1	20.0	p.d. 9	d. 5	d. 3	d. 1, 2	d. 2, 3	d. 2, 3	d. 4
German 2	22.6	v.d. 2	d. 7, 8	d. 5	d. 5	d. 5
South Wales 7	24.7	s. 11	d. 7, 8	d. 6	d. 7	d. 2, 3	d. 2, 3	d. 6
South Wales 2	25.5	v.d. 1	d. 1	d. 4	d. 6	d. 1	d. 1	d. 1
Kent 1	25.5	p.d. 6	d. 3	s. 9	s. 8, 9	d. 9
Durham 16	26.8	p.d. 5	s. 10	s. 10	s. 4	d. 5
Durham 1	29.2	p.d. 3	s. 9	s. 11	s. 8, 9	d. 4	d. 8
Somerset 1 W.D. b	29.8	d. 7 * *	s. 5 *	d. 1
Somerset 1 W.D. a	30.1	p.d. 4	d. 2	d. 2 *	d. 3, 4 * *

Notes: *par. d.*, particularly dangerous; *v.d.*, very dangerous; *d.*, dangerous; *p.d.*, possibly dangerous; *s.*, safe. Relative order of decreasing danger: 1, 2, 3 . . . 12.

* Question as to which Somerset coal was used.

exceptions. The reasons for the inconsistencies in order of dangerous expanding characteristics shown by different methods for the same coals have a partial explanation in the peculiar properties of certain coals. The rapid rate of heating in the small-scale tests tends to give misleading results for certain coals of strong swelling power or for those that became exceedingly plastic. Removal of the finer sizes or the use of more coarsely crushed coal gave better results in the modified small-scale Koppers test, the Nedelmann test, and the Koppers large-scale swelling test, although this practice was found to be unnecessary in the Baum-Heuser test. No satisfactory reason can be advanced for this difference, because in the Baum-Heuser test, despite the fact that it uses an 80-gram charge of coal smaller than 1 millimeter, rates of heating of 40 and 13° C per minute are found at the bottom and top, respectively.

Mott and Spooner¹⁶¹ suggested that

in coking very strongly swelling coals coarse crushing (100 percent passing $\frac{1}{2}$ inch) is desirable and that, if the bulk density requires to be controlled, such coals should be wet washed and charged wet, when a bulk density of 750 kilograms per cubic meter will probably not be exceeded. Strongly swelling coals, in fact, do not need crushing (as do weakly swelling coals) to yield a strong coke, and

the control of their size and bulk density will serve to control the volume of the free space in the oven, a factor of importance in obtaining the maximum yield of crude benzole.

SUMMARY

Reference to the reviews of individual investigations indicates that the present status of methods for measuring the plastic, agglutinating, agglomerating, swelling, and swelling pressure properties, as well as other closely related characteristics, of coals justifies careful further investigation. Perhaps the latest proposed American and British methods for determining the agglutinating value and the Canadian method for estimating the agglomerating value of coal have now reached states of perfection beyond which little further improvement can be expected. Methods for measuring plastic properties of coals need a thoroughly coordinated, cooperative study by different laboratories with a view to ultimate standardization of some one or more of the existing test methods, or, if found desirable, of a modified or new method. The same argument applies with equal emphasis to the methods now used for determining expansion and expansion pressures of coals. The American trend toward large test units and large-scale installations using two-sided heating appears most promising.

CHAPTER 7

PHYSICAL PROPERTIES OF COALS *

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A beginning has been made in the measurement of certain physical properties of coal which have long been studied in many minerals and rocks. Because the properties of coal vary with the composition and condition of the vegetation at the time of its accumulation and burial—type—and with the modifications of progressive alteration after burial—rank,¹ the selection and precise definition of material for investigation are difficult. Furthermore, kind and quantity of mineral matter, amount and state of water, and rapidity of oxidation on exposure to air are serious obstacles to accurate physical measurement. These limitations and the qualifications which they introduce must be borne in mind when the results of determinations of physical properties of coal are reviewed.

The present report summarizes the literature dealing with specific gravity, electrical conductivity, thermal conductivity, specific heat, index of reflection, index of refraction, and absorption and diffraction of X-rays, using coal from all parts of the world. The discussion is primarily

concerned with the physical properties of coal considered as a substance rather than as an aggregate of particles. Effective values of the physical properties of aggregates must be given special study. This important aspect of the problem of the physical attributes of coal is touched upon when it seems appropriate to do so; but since knowledge of the coal substance making up an aggregate logically precedes a knowledge of the properties of the aggregate, the viewpoint of the coal substance is emphasized.

SPECIFIC GRAVITY

Coals exhibit a considerable range of specific gravity because of differences in kind and quantity of mineral matter, in moisture content, in type, and in rank.

Definitions. *Specific gravity* is density relative to that of water at some specified temperature, usually 4° C. It is dimensionless. *Apparent specific gravity* is the specific gravity of lump coal, with inherent moisture, mineral matter, and air in pore spaces included. *True specific gravity* is the specific gravity of the coal substance, free of air and uncombined water but containing mineral matter. Adopting the

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¹ Hickling, G., *Colliery Guardian*, 144, 401-4 (1932).

usage of Nebel,² *unit specific gravity* is specific gravity corrected for moisture, air, and mineral matter.

Methods of Determination. The hydrometer,³ the Jolly balance,² and the Westphal balance are commonly used for determining the apparent specific gravity of lumps of coal. The lumps must be surface-dried in order to obtain meaningful results. The true specific gravity of coal may be determined by means of some modification of the specific-gravity bottle or pycnometer, in which pulverized moisture-free coal is boiled to free it of air.^{4, 5} In all such methods, the specific gravity is the ratio of the weight of the sample in air to its loss of weight in water. For greater accuracy, or if the test liquid is other than water, this ratio is multiplied by the specific gravity of the test liquid at the temperature of observation.

Details of technique have not been entirely agreed upon. In at least one investigation the procedure of crushing and boiling air-dried coal was undertaken to obtain "apparent" (containing moisture but not air) specific gravity.⁶ True specific gravity was then calculated by use of an appropriate factor based on the assumption that the specific gravity of the total moisture contained in the coal is unity.

As a guide to good practice in the direct determination of true specific gravity, it

may be appropriate to note the very considerable attention given to the accurate determination of the true specific gravity of coke. Both the American Society for Testing Materials⁷ and the British Standards Institution⁸ published detailed specifications, and a number of investigators⁹ have contributed toward a satisfactory solution of the problem. An exacting study has been made by Hiles and Mott,¹⁰ who concluded, contrary to the opinion of some, that water is the most suitable pycnometer fluid and that minus 60-mesh is sufficiently fine to crush the coke. It has been reported¹¹ that helium and other gases have been used as pycnometer fluids.

The specific gravity of the pure coal substance, *unit specific gravity*, cannot be directly determined but may be approximated on the basis of simplifying assumptions. For example, the approximate increase of 0.01 in apparent specific gravity for each percent increase of ash, which has been noted by several workers,^{4, 12, 13, 14}

⁷ *Am. Soc. for Testing Materials, Standard D167* (1924), 5 pp.

⁸ *Brit. Standards Inst., Standard 735*, 56 (1937).

⁹ Rose, H. J., *Ind. Eng. Chem.*, **14**, 1047-9 (1922). Selvig, W. A., and Parker, W. L., *Chem. & Met. Eng.*, **28**, 547-50 (1923). Neumann, B., Gross, W., Kremser, L., and Schmidt, J., *Brennstoff-Chem.*, **15**, 161-5 (1934).

¹⁰ Hiles, J., and Mott, R. A., *Fuel*, **16**, 64-71 (1937).

¹¹ *Résumé of Current Research in Coal and Coal Utilization*, Bituminous Coal Research, Inc., Washington, D. C., 1936, p. 10. Palvelev, V. T., *Bull. acad. sci. U.R.S.S., Classe sci. Tech.*, **1939**, No. 4, 79-88; *Chem. Abs.*, **34**, 7575 (1940). Smith, R. C., Jr., and Howard, H. C., *Ind. Eng. Chem.*, **34**, 438-41 (1942).

¹² Seyler, C. A., *Practical Coal Mining*, Graham Bros., London, 1909, p. 80.

¹³ Fermor, L. L., *Records Geol. Survey India*, **60**, 313-57 (1928); *Fuel*, **8**, 16-29 (1929).

¹⁴ Lawall, C. E., and Holland, C. T., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 100-16 (1932).

² Nebel, M. L., *Univ. Illinois Eng. Exp. Sta., Bull.* **89** (1916), 49 pp.

³ Stanton, F. M., Fieldner, A. C., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper* **8** (1939), 59 pp.

⁴ Strahan, A., and Pollard, W., *Mem. Geol. Survey of England and Wales*, 2nd Ed., 1915, p. 12.

⁵ Drakeley, T. J., and Hepburn, J. R. I., *J. Soc. Chem. Ind.*, **43**, 134-7T (1924). Moore, E. S., *Coal*, John Wiley & Sons, New York, 1940, p. 6.

⁶ Turner, H. G., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 330-43 (1934).

may be extrapolated to zero ash content as a first approximation.¹³ However, this relationship is not rigorous and must be modified for coals containing considerable amounts of iron compounds. It is sometimes used to secure rapid estimates of ash content at coal washeries or in the field.

Turner⁶ suggested an expression for dry, ash-free specific gravity on the basis of an assumption that ash is the quantitative equivalent of mineral matter, with a specific gravity of 2.7. Although this is undoubtedly a close approximation, generally, to unit specific gravity, the latter can be approximated still more closely by correcting for the inequality of ash and mineral matter.^{15, 16}

For most coals, mineral-matter content is of the order of 15 percent larger than ash content.^{17, 18} A usually more accurate value may be obtained with the aid of the widely used Parr expression¹⁹

Mineral matter

$$= 1.08 \times \text{Ash} + 0.55 \times \text{Sulfur}$$

or of one of several suggested modifications.^{19, 20} The following expression has been suggested specifically for English coals by King and his associates:²¹

¹³ Brinsmaid, W., *J. Ind. Eng. Chem.*, **1**, 65-8 (1909). Mayer, K., *Brennstoff-Chem.*, **10**, 377-82 (1929). Stansfield, E., and Sutherland, J. W., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 614-26 (1929).

¹⁶ Schuster, F., *Gas- u. Wasserfach*, **74**, 629-33 (1931).

¹⁷ Purdon, A., and Saggirs, S., *Fuel*, **12**, 40-6 (1933).

¹⁸ Thiessen, G., *Illinois State Geol. Surv., Rept. Investigations* **32**, 27-39 (1934).

¹⁹ Parr, S. W., and Wheeler, W. F., *Univ. Illinois Eng. Exp. Sta., Bull.* **37** (1909), 68 pp.

²⁰ Fieldner, A. C., and Selvig, W. A., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 597-613 (1930).

²¹ King, J. G., Maries, M. B., and Crossley, H. E., *J. Soc. Chem. Ind.*, **55**, 277-81T (1936).

$$\text{Mineral matter} = 1.09 \times \text{Ash} + 0.5 \times$$

$$\begin{aligned} & \text{Pyritic sulfur} + 0.8 \times \\ & \text{CO}_2 - 1.1 \times \text{Sulfates} \\ & \text{in Ash} + \text{Sulfates origi-} \\ & \text{nally present in the} \\ & \text{coal} + 0.5 \times \text{Total} \\ & \text{chlorine} \end{aligned}$$

where all values are expressed in percentages of the dry coal. Modifications of these formulas may be required for specific coals, depending mainly on the forms in which the sulfur and the carbonates occur.

Perhaps the nearest approach to direct determination of mineral-matter content involves the visual identification and quantitative estimation of the minerals associated with the coal. This laborious procedure was completely carried out by Ball²² for one Illinois coal sample.

In addition to an estimate of quantity of mineral matter, an estimate of mean specific gravity of mineral matter is required for computing unit specific gravity. Mean specific gravity of mineral matter may be approximated more or less closely from a knowledge of pyritic sulfur (or, less satisfactorily, of total sulfur) and of total mineral matter by using 5.0 for the specific gravity of pyrite and 2.7 for that of the other minerals in coal. Unit specific gravity is then given by

$$\frac{(100 - p)ab}{100b - ap}$$

where a = true specific gravity of coal, including mineral matter.

b = average specific gravity of mineral matter.

p = percentage by weight of mineral matter in coal.

Based essentially on the above expression, specific-gravity assay methods have been suggested for the rapid determination

²² Ball, C. G., *Illinois State Geol. Surv., Rept. Investigations* **33** (1935), 106 pp.

of incombustible matter in mixtures of coal and rock dust²³ and of the ash content and calorific value in coal of any constant type,²⁴ such as would be encountered in control testing at most coal-preparation plants. The methods assumed that the material tested is a mechanical mixture of two components, each of constant and known specific gravity. By measuring the specific volume of the mixture, the percentage of each component could be estimated by computation or by reference to an appropriate calibration table. In Lategan's discussion the calibration table was extended to cover calorific values. It may be remarked that both these papers inadvertently stated that the above assumption leads to the linearity of content by weight of the heavier component (rock dust in the discussion by Fieldner, Selvig, and Osgood; ash or mineral matter in that by Lategan) with specific gravity of the mixture. This assumption actually leads to a relationship between content by weight of the heavier component and specific gravity that is curvilinear, being concave toward the specific-gravity axis.^{13, 25} However, the curvilinearity is so slight up to 30 or 40 percent of the heavier component that most data on coal appear to bear a linear relationship, as has been noticed by several investigators.^{4, 12, 13, 14, 23, 24} Rigorous linearity would imply systematic variations in the specific gravity of the coal substance or of the mineral matter (or ash), or a swelling in total volume when the two are combined in varying concentrations.

²³ Fieldner, A. C., Selvig, W. A., and Osgood, F. D., *U. S. Bur. Mines, Tech. Paper 144* (1918), 36 pp.

²⁴ Lategan, P. N., *Fuel*, **6**, 447-8 (1927).

²⁵ Whitaker, J. W., *Trans. Inst. Mining Engrs.*, **64**, 191-202 (1922). Drakeley, T. J., and Hepburn, J. R. I., *J. Soc. Chem. Ind.*, **43**, 277-8T (1924); *Colliery Guardian*, **128**, 744 (1924).

Freshly mined coal is usually assumed to be saturated with moisture, most of which is probably held mechanically in the pore space.²⁶ The apparent specific gravity of a given coal usually decreases as the coal loses moisture,^{2, 14, 27, 28} but, if the coal is soaked in water for some hours before apparent specific gravity is determined, the value obtained closely approximates that of the coal as mined.^{2, 26} Variables of rank, type, and ash content being equal, coals having higher moisture content in the fresh condition usually have lower apparent specific gravity.²⁶

Variations in specific gravity inherently due to type differences have been little explored. Vitrain is usually found to have the lowest apparent specific gravity, which is probably a reflection of its relatively low ash content. The apparent specific gravities of clarain and of durain²⁹ are generally but not always higher. These types are composed of a variety of plant materials and must be more carefully classified before significant variations are apparent. It has been observed that spore exines found in both these types of coal have somewhat lower³⁰ apparent specific gravity than the other plant remains occurring with them.

Lange³¹ collected 28 instances in which apparent specific-gravity data on bright and dull coals and fusain were directly comparable, together with complete proximate and ultimate analyses on 16 such sets

²⁶ McMillan, E. R., and Bird, B. M., *Univ. Wash. Eng. Exp. Sta., Bull.* **28** (1924), 234 pp.

²⁷ Drakeley, T. J., and Jones, W. O., *J. Soc. Chem. Ind.*, **42**, 163-6T (1923).

²⁸ Fermor, L. L., *Records Geol. Survey India*, **62**, 189-228 (1930); *Fuel*, **9**, 246-65 (1930).

²⁹ Fermor, L. L., *Records Geol. Survey India*, **63**, 358-77 (1930).

³⁰ Macrae, J. C., and Wandless, A. M., *J. Soc. Chem. Ind.*, **55**, 15-9T (1936).

³¹ Lange, T., *Schriften aus dem Gebiet der Brennstoff-Geologie*, Ferdinand Enke, Stuttgart, 1929, pp. 55-127.

of three and proximate analyses on 12 sets on a dry basis. Fusain exhibited the highest specific gravity in all cases but two, the average values for the bright coal, the dull coal, and the fusain being 1.293, 1.306, and 1.519, respectively. The respective average dry ash contents were 1.52, 4.94, and 9.00 percent, indicating that the high apparent specific gravity of fusain was due to a certain extent to mineral matter associated with it, but even very pure fusain,³² and fusain on a dry, ash-free basis,³³ have been found to have a distinctly higher specific gravity than the associated coal components.

On the basis of the observed linear relationship between apparent specific gravity and ash content of certain Indian coals studied by him, Fermor³² concluded that coals of the "vitrain-durain series" may be considered colloid systems of the suspensoid type, in which vitrain is the dispersion medium, mineral matter a fine dispersed phase, and vegetable detritus a coarse dispersed phase, and that vitrain itself is composed of moisture and moisture-free vitrain in a colloidal relationship.²³ However, these deductions are not altogether obvious from his data, since linearity of specific gravity and composition by weight of a two-component mixture are not generally accepted as a sufficient condition for a colloidal system.³⁴

Fermor found no consistent correlation relating the ash-free specific gravity³⁵ of the vitrains and durains he studied with volatile matter, fixed carbon, or fuel ratio, but he did note that, for any given coal,

ash-free specific gravity increased with moisture either regularly or in steps.^{28, 29}

Specific-gravity differences due to rank may largely obscure the correlation of ash or mineral-matter content with apparent specific gravity when a number of coals of different rank are considered together. This is illustrated by a series of 70 tests on various American coals made by the United States fuel-testing plant at the Louisiana Purchase Exposition,³⁶ in which there is a nearly complete lack of correlation of apparent specific gravity with either ash or sulfur content. Varying moisture content probably contributed to the scatter of the data.

Coals of higher rank tend to have higher specific gravity, as is fairly apparent in the series representing a wide range of rank difference shown in Table I.³⁷ The increase in specific gravity (probably apparent specific gravity, although the authors did not say) may be accounted for by progressive breaking up of the hydrocarbons, loss of the lighter atomic groups, and rearrangement into heavier groups during coalification.

Washability or float-and-sink testing is a widely employed laboratory technique based on differences in the apparent specific gravity of coal from a single source and of the associated impurities. The coal is usually separated into several fractions by heavy liquids of various known specific gravities, chosen in the critical range of separation of coal and refuse. Water solutions of zinc chloride are commonly used for the coarse sizes,^{26, 38, 39} and organic so-

³² Lange, T., *Z. oberschles. berg- u. hüttenmänn. Ver. Katowice*, **67**, 334-7 (1928).

³³ Wandless, A. M., and Macrae, J. C., *Fuel*, **13**, 4-15 (1934).

³⁴ Wintgen, R., *Kolloid-Beihfte*, **7**, 251-82 (1915).

³⁵ Obtained by the deduction of 0.01 from apparent specific gravity for each percent of ash on an as-received basis.

³⁶ Lord, N. W., *U. S. Geol. Survey, Bull.* **323** (1907), 49 pp.; *U. S. Bur. Mines, Bull.* **28** (1911), 51 pp.

³⁷ Hoffmann, E., and Jenkner, A., *Glückauf*, **68**, 81-8 (1932); *Fuel*, **12**, 98-106 (1933).

³⁸ McMillan, E. R., and Bird, B. M., *U. S. Bur. Mines, Rept. Investigations* **2570** (1924), 12 pp.

³⁹ Callen, A. C., and Mitchell, D. R., *Univ. Illinois Eng. Exp. Sta., Bull.* **217** (1930), 114 pp.

TABLE I

ASH, VOLATILE MATTER, SPECIFIC GRAVITY, AND ULTIMATE
ANALYSIS OF COALS OF DIFFERENT RANK ³⁷

Coal	Ash percent	Volatile Matter percent	Specific Gravity	Carbon percent	Hydrogen percent	Sulfur percent	Nitrogen plus Oxygen percent
Brassert flame coal	3.20	40.58	1.31	79.10	6.16	1.96	10.48
Prosper gas coal	1.45	25.89	1.29	84.32	4.88	0.87	8.50
König Ludwig fat coal	8.10	21.45	1.34	83.94	3.58	1.07	4.21
Langenbrahm anthracite	1.97	8.70	1.35	88.72	3.86	0.76	5.59
Pennsylvania anthracite	3.48	4.10	1.45	90.03	2.59	0.75	3.15
Italian anthracite	7.01	8.87	1.76	87.45	1.30	0.28	3.96
Trieben graphite	2.45	4.90	1.90	94.46	0.56	0.24	2.20

lutions, such as mixtures of benzene, carbon tetrachloride, and bromoform, for the fine coal.^{39, 40} The test data are most readily interpreted through the construction of washability curves.⁴¹ This information is of prime importance in planning appropriate preparation processes for a given coal, since most coal-cleaning processes depend to a large extent upon differences in specific gravity for the separation of clean coal from refuse.^{39, 42} (See Chapter 16.)

Apparent specific gravity is a variable of obvious importance in connection with bulk density of broken coal,⁴³ although its effect is greatly modified by the voidage characteristic of the size distribution and of the degree of segregation of the broken coal.

⁴⁰ Bird, B. M., and Messmore, H. E., *U. S. Bur. Mines, Rept. Investigations* 2586 (1924), 4 pp.; *Univ. Wash. Eng. Exp. Sta., Bull.* 46 (1928), 36 pp. Hall, P. E., *J. Chem. Met. Mining Soc. S. Africa*, **32**, 174-81 (1932), **34**, 263-9 (1934), **35**, 183-4 (1935).

⁴¹ Bird, B. M., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 82-111 (1928), *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 721-35 (1931). Coe, G. D., *U. S. Bur. Mines, Circ.* 7045 (1938), 10 pp.

⁴² Chapman, W. R., and Mott, R. A., *The Cleaning of Coal*, Chapman and Hall, London, 1928, 680 pp. Yancey, H. F., and Fraser, T., *U. S. Bur. Mines, Bull.* 300 (1929), 259 pp. Yancey, H. F., and Porter, C. B., *U. S. Bur. Mines, Tech. Paper* 536 (1932), 18 pp. Gaudin, A. M., *Principles of Mineral Dressing*, McGraw-Hill Book Co., New York, 1939, 554 pp.

⁴³ Flagg, S. B., *U. S. Bur. Mines, Tech. Paper* 184 (1918), 11 pp.

This is a little-explored field, but some thought-provoking discussions have appeared.⁴⁴

ELECTRICAL CONDUCTIVITY

Electrical conductivity may be defined as the reciprocal of electrical resistivity, where the latter is measured by the resistance of a body of unit length and unit cross-sectional area. The unit of electrical conductivity is the mho per centimeter; that of electrical resistivity is the ohm-centimeter. For high resistivities the unit megohm-centimeter is sometimes used, equivalent to 10⁶ ohm-centimeters.

The electrical conductivity of coal and coke has been the subject of a number of investigations within recent years. Extensive geophysical field studies have been undertaken by government surveys and private agencies in prospecting for coal,^{45, 46} and some of the field investigations have been preceded by laboratory experiments for the purpose of evaluating the resistivity

⁴⁴ Furnas, C. C., *U. S. Bur. Mines, Bull.* 307, 82 (1929). Leven, K., *Glückauf*, **67**, 770-2 (1931); *Fuel*, **10**, 369-71 (1931). Dummett, G. A., and Greenfield, G. J., *Colliery Guardian*, **148**, 674-7, 722-4 (1934). Rosin, P. O., *Trans. Inst. Chem. Engrs. London*, **15**, 167-92 (1937). Koepfel, C., *Glückauf*, **73**, 369-78 (1937); *Fuel*, **17**, 10-8 (1938).

⁴⁵ Hawkins, R. H., *Trans. Am. Inst. Mining Met. Engrs.*, **110**, 76-120 (1934).

⁴⁶ Ewing, M., Crary, A. P., Peoples, J. W., and Peoples, J. A., Jr., *ibid.*, **119**, 443-83 (1936).

characteristics of the coals and their associated beds. The data are not always comparable, however, as the conditions of laboratory work sometimes differed significantly.

In examining the work of various investigators on the electrical conductivity of coal, a distinction must be drawn between tests on coal blocks, inclusive or exclusive of mineral matter, and tests on aggregates of coal particles. The majority of investigations deal with the aggregates, and it must be remembered that for such samples values for electrical conductivity or resistivity are not correctly referred to coal (or lignite or coke) but rather to aggregates of these particles. Such "effective" values are strongly affected by particle-size distribution and by degree of packing and must be viewed warily lest they be of *ad hoc* value only.

Wet lignites have been found by Hawkins⁴⁵ to be very good conductors of electricity, relative to most coals and associated materials. Of the silts, lignites, and clays he studied, a wet lignite was the best conductor, having a conductivity approximately twelve times that of the most resistant clay. For the most part, the conductivities of lignite and clay were in a ratio of about 3 to 1. Resistivity was found to be strongly dependent upon moisture content, as indicated by ohm-centimeter values of 900 for wet lignite and 3,500 for lignite dried to the crumbling point. Details of the laboratory work were not given, but it was stated that an electrical current was passed through shaped bars of lignite and through cylindrical blocks of clay packed in glass tubing.

Higher-rank coal exhibits definite anisotropism with reference to the passage of electricity, as Sinkinson⁴⁷ pointed out for

anthracite. Using two polished centimeter cubes, he noted resistances of 789 and 992 ohms when the current was passed parallel to the coal laminae, and 4,509 and 5,090 ohms when the current passed perpendicular to them. This characteristic is highly developed in graphites, the resistivity normal to the principal axis of the crystallites being of the order of one hundred times greater than that parallel to the axis.⁴⁸

Ewing and his associates⁴⁶ were concerned with the resistivity of anthracite and its associated rocks in the western middle anthracite basin of Pennsylvania. In their laboratory work they explored dry anthracite blocks by two methods: (1) a duplication to a reduced scale of the standard four-electrode method used in the field; and (2) a determination of the potential drop at intervals along a prism of anthracite 5 to 10 centimeters long and 1 to 2 centimeters thick. Orientation of coal laminations was not reported. One series of 15 blocks averaged 1.2×10^{-4} megohm-centimeter, ranging from 0.7×10^{-4} to 2×10^{-4} megohm-centimeter. A second series of 6 blocks averaged $2,100 \times 10^{-4}$ megohm-centimeter, and a third set of 4 blocks, collected fairly close together in the Mammoth Seam near Shamokin, resulted in determinations of 1, 60, 100, and 600 megohm-centimeters. These are extremely wide variations. Three specimens of bituminous coal from New River, West Virginia, yielded results of 60, 100, and 150 megohm-centimeters. They were reported as having 27 percent volatile matter, 69 percent fixed carbon, 4 percent ash, and 0.7 percent sulfur, on the dry basis. The authors suggested that variation in resistivity may be concomitant with variations in volatile-matter content, but the evi-

⁴⁷ Sinkinson, E., *Ind. Eng. Chem., Ind. Ed.*, **20**, 862-5 (1928).

⁴⁸ Washburn, G. *Ann. Physik*, **48**, 236-50 (1915).

dence presented hardly warrants a definite conclusion.

Experiments on the electrical conductivity of aggregates of particles were reported by Sinkinson⁴⁹ in 1925, in which definite changes in conductivity were found to take place as pulverized bituminous coal and anthracite were heated in a closed vessel. In this work Sinkinson buried two electrodes approximately 1 centimeter apart in the coal to be tested, which was then slowly heated in an electric furnace of special design. The temperature at which, under the conditions of the experiment, a perceptible current would flow between the electrodes was taken as a measure of conductivity. This critical conducting temperature apparently was fairly sharp and reproducible. It was observed that this temperature was somewhat higher for strongly coking coal than for poorly coking coal, and, for anthracite, the range of reported results extended from 425 to 570° C. Other experiments indicated that the conduction between the electrodes is due to free carbon liberated by the thermal decomposition of the hydrocarbon gases evolved during heating. In 1938, Sinkinson and Ganz presented some further data obtained by this method.⁵⁰

Adopting a different approach from that in the work reported in 1925, Sinkinson⁴⁷ developed a cell suitable for measuring directly the resistance of any conducting powder, in which the test cell is operated simultaneously with a standard cell. In this work he measured the electrical resistance of 1 gram of minus 48-mesh coal, compacted in a 1-centimeter glass cylinder. Contact resistance between coal and electrodes was determined and

subtracted, but since distances between electrodes during the tests were not reported, the results cannot be converted from ohmic resistance to resistivity. Five Pennsylvanian and two Scottish anthracites and semianthracites, quite similar as to proximate analysis, were tested with results ranging from 75 to 6×10^6 ohms. Part of the wide variation may be due to the extreme effect of particle size on resistance, as disclosed in preliminary work with the cell. It is interesting to note that mixtures of graphite and calcium carbonate in varying percentages began to increase sharply in resistance when the graphite content fell below 15 percent. In this connection the interested reader may wish to compare the work of Aryakos,⁵¹ who noted a logarithmic dependence of conductivity on the composition of a mixture of equally ground materials.

The possibility of using the property of electrical conductivity as a measure of the degree of carbonization of coke was investigated by Koppers and Jenkner⁵² with encouraging results. For this work they used a conductivity cell essentially like that of Sinkinson,⁴⁷ except that no standard cell was operated concurrently with it. Although they noted an effect on conductivity due to particle size, Koppers and Jenkner standardized on 70×100 mesh-per-centimeter particles, under a pressure of 150 atmospheres (155 kilograms per square centimeter). Ten low-ash coals, ranging in volatile matter content from 7 to 40 percent, were carbonized at 950° C. The results, expressed as resistivity, ranged from 0.0403 to 0.1561 ohm-centimeter, the lower values being associated with the better cokes. Resistivity

⁴⁹ Sinkinson, E., *Ind. Eng. Chem., Ind. Ed.*, **17**, 27-31 (1925).

⁵⁰ Sinkinson, E., and Ganz, J., *ibid.*, **30**, 1419 (1938).

⁵¹ Aryakos, G. Y., *J. Tech. Phys. U.S.S.R.*, **4**, 307-12 (1934).

⁵² Koppers, H., and Jenkner, A., *Arch. Eisenhüttenw.*, **5**, 543-7 (1932).

was found to decrease markedly with carbonizing temperature, as indicated by six tests with the best coking coal of the first series, at temperatures from 400 to 1,200° C. It was concluded that ash content, within its usual limits, is of only slight importance.

Myer,⁵³ in an examination of certain physical properties of selected coals, noted that anthracite particles exhibited resistances of the order of one-hundredth that of the low-volatile bituminous coals tested, and of the order of one-thousandth that of an Indiana high-volatile bituminous coal. A conductivity cell of the same essential type as that of Hoffmann and Jenkner was used in this investigation. Resistance was found to decrease with increased pressure, becoming sufficiently constant at 10 kilograms per square centimeter to warrant standardizing on this figure. Samples weighing 2 grams were used, and results were reported in terms of ohmic resistance rather than resistivity. Results for 14 dried anthracites ranged from 5,600 to 44,900 ohms, with an average of 16,530 ohms. No particular correlation with volatile matter is evident. A series of seven samples of anthracite from Shamokin was notably higher in resistance, ranging from 110×10^4 to $2,800 \times 10^4$ ohms, which should be compared with the results of Ewing and his associates⁴⁰ on Shamokin anthracite. An Indiana high-volatile bituminous coal yielded a value of $4,750 \times 10^4$ ohms; a charcoal, 46 ohms; a coke, 0.37 ohm; and a graphite, 0.173 ohm. Myer found that all coal samples after being carbonized at 950° C exhibited uniformly low resistances, of the order of 0.77 ohm, suggesting that the residual carbon content of all coals tested under these conditions was very much the same.

⁵³ Myer, J. L., *Am. Inst. Mining Met. Engrs., Tech. Pub.* 482 (1932), 19 pp.

Davis and Auvil⁵⁴ studied the electrical conductivity of dried cokes from ten widely distributed American coking coals, coked in the special test retort developed by the United States Bureau of Mines and the American Gas Association. Their conduc-

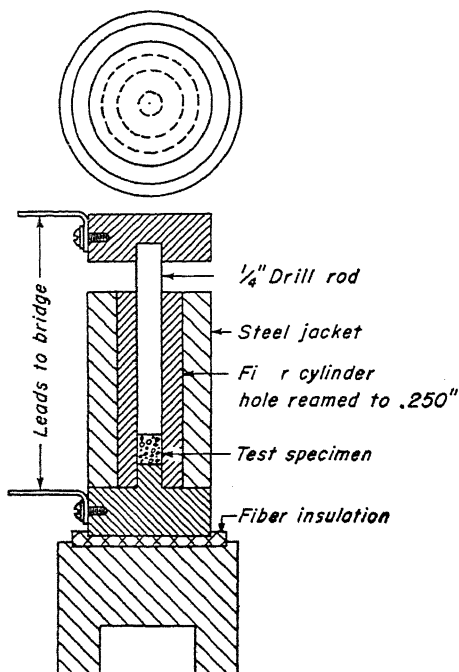


FIG. 1. Electrical conductivity cell.⁵⁴

tivity cell (Fig. 1) was similar in principle to that of Koppers and Jenkner⁵² and of Myer,⁵³ but a much higher pressure, 60,000 pounds per square inch (4,220 kilograms per square centimeter), was found to be desirable. With proper technique good reproducibility was achieved. Approximately $\frac{1}{2}$ gram of 150- to 200-mesh coke particles was used. For cokes prepared at carbonizing temperatures ranging from 600 to 1,100° C, those from Illinois No. 6 coal

⁵⁴ Davis, J. D., and Auvil, H. S., *Ind. Eng. Chem.*, 27, 1196-200 (1935).

TABLE II
ELECTRICAL RESISTIVITY OF VITRAIN, CLARAIN, AND FUSAIN ⁵⁵

Laboratory No.	Material	Rank	Coal Seam	Locality	Resistivity		Analytical Data (Dry Basis)							Btu per Pound
					Dry	Wet	Ash	Volatile Matter	Fixed Carbon	Sulfur				
										Sulfate	Pyritic	Organic	Total	
							per-cent	per-cent	per-cent	per-cent				
C-1097	Vitrain	Lignite		Hernando, Miss.	megohm-centimeter		per-cent	per-cent	per-cent					9,965
C-1048	Vitrain	Subbituminous B		Lafayette, Colo.	>300	0.169	5.6	48.4	46.0					12,765
C-1090	Vitrain	High-volatile bituminous B		Booneville, Ind.	>300	0.51	3.0	37.7	59.3					
C-1703	Vitrain	High-volatile bituminous C	Herrin (No. 6)	Farmington, Ill.	>300	0.274	0.8	44.7	54.5					14,266
C-1704	Vitrain	High-volatile bituminous C	Colchester (No. 2)	Roanoke, Ill.	>300	0.415	1.4	40.0	59.2					14,376
C-1602	Vitrain	High-volatile bituminous A	Harrisburg (No. 5)	Harrisburg, Ill.	>300	0.148	1.7	39.7	58.9					14,388
C-1601	Vitrain	High-volatile bituminous A	Harrisburg (No. 5)	Gilsonia, Ill.	>300		1.7	36.5	61.8					14,431
C-1608	Vitrain	Medium-volatile bituminous	Lower Hartshorne	Hartshorne, Okla.	>300	0.022	2.3	41.0	57.3					14,763
	Clarain	High-volatile bituminous B		Booneville, Ind.	>300			24.1	73.6					15,363
	Clarain	High-volatile bituminous C	Herrin (No. 6)	Farmington, Ill.	>300									
	Clarain	High-volatile bituminous A	Harrisburg (No. 5)	Harrisburg, Ill.	>300									
C-350	Fusain		Herrin (No. 6)	Elkville, Ill.	ohm-centimeter		15.2	22.0	62.8	0.06	1.75	0.53	2.34	12,122
C-336	Fusain		Rock Island (No. 1)	Alpla, Ill.	1,680		7.3	16.9	75.8	0.26	3.12	0.73	4.11	13,659
C-330	Fusain		Colchester (No. 2)	Winnington, Ill.	82		11.6	21.5	66.9	0.04	4.99	0.50	5.53	13,285
C-338	Fusain		Springfield (No. 5)	Crescent, Ill.	15		5.2	18.0	76.8	0.03	0.45	0.73	1.21	14,184
C-353	Fusain		Harrisburg (No. 5)	Harrisburg, Ill.	7		5.9	12.7	81.4	0.01	0.68	0.22	0.91	14,018

yielded systematically high results whereas those from the Sewell Seam of West Virginia were consistently low, the respective values at a carbonizing temperature of 800° C being 0.2060 and 0.0316 ohm-centimeter. A large decrease in resistivity occurred with increase in carbonizing temperature, such that the average value for coke made at 600° C was about 370,000 times that for coke made at 1,100° C, for the five coals tested. It was concluded that the kind and quantity of volatile matter in the coke affect its resistivity to a marked degree. A logarithmic relationship fits the data fairly well, although the constants of the expression for carbonizing temperatures at and above 800° C are different from those below 800° C.

An exactly similar cell and similar test procedure were used by McCabe⁵⁵ in determining the resistivity of 150- by 200-mesh samples of the banded ingredients. The resistivities of all samples of moisture-free vitrain and clarain were greater than 300 megohm-centimeters (Table II), which places them in the class of materials loosely termed "nonconductors." Fusain, in contrast to vitrain and clarain, exhibited low resistivity. With one exception, the resistivity of fusain decreased with a decrease in volatile matter. Resistivity values of dry fusain were lower than those for wet vitrain.

Davis and Younkings⁵⁶ made use of the higher electrical conductivity and higher electrostatic capacity of fusain to separate it from associated bone coal and mineral matter after removing the components of lower specific gravity by centrifuging the sample in a mixture of gasoline and carbon tetrachloride of 1.40 to 1.45 specific gravity.

⁵⁵ McCabe, L. C., *Fuel*, **16**, 267-80, 309-16 (1937).

⁵⁶ Davis, J. D., and Younkings, J. A., *Fuel*, **8**, 438-40 (1929).

Utilizing the electrical conductivity of a core of coke, the Detroit Edison Company developed a process for the coking of coal by electricity, for which many advantages have been claimed.⁵⁷ The experimental retort had a capacity of 30 tons of coal, which was fed into a vertical cylinder 40 feet long and 6 feet in diameter, around a comparatively small core of coke particles. The heat developed in passing electricity through the core carbonized the immediately surrounding coal layer, which in turn became a conductor and permitted the heating of following layers. Coking thus proceeded from the inside out.

THERMAL CONDUCTIVITY

Thermal conductivity may be defined as time rate of transfer of heat by conduction across unit area for unit temperature gradient. Its units in the cgs system are calories per second, per square centimeter, per "degree Centigrade per centimeter thickness," which are the units used in this report. The cgs units may be converted to Btu per hour, per square foot, per "degree Fahrenheit per foot thickness" by multiplying the figures given by 241.9.

The experimental determination of the thermal conductivity of coal as a substance has been largely neglected in favor of that of coal as an aggregate of particles, both because of more difficult experimental conditions surrounding the former and because practically all uses of coal involving the application of heat are concerned with coal as masses of particles. Furthermore, the thermal conductivity of a mass of particles of the general nature of coal is dependent only in small part on the conductivity of the substance of the particles and depends to a far greater extent on radia-

⁵⁷ Stevens, H., *Proc. Fuel Eng. Conf.*, **3**, 413-45 (1936); *Scientific American*, **157**, 270-2 (1937).

tion from particle to particle, which in turn is a function largely of temperature and physical geometry.⁵⁸ The nature of the gas filling the free spaces between grains is also of considerable importance.⁵⁹ In view of these considerations, the relative lack of attention to the thermal conductivity of coal as a substance is understandable.

The thermal conductivity of the coal substance was investigated by Sinnatt and Macpherson⁶⁰ in 1922, using the compound bar method. In this work, a 59-centimeter brass bar was cut in two in a plane perpendicular to the long axis, and discs of coal from 1 to 2 millimeters thick and about 1.6 centimeters in diameter were placed between the halves of the bar. Steam was applied to one end of the bar and cold water to the other; after equilibrium had been established, the temperature gradient along the bar was investigated by means of thermocouples. The thermal conductivity could be computed from the resulting data. A total of twelve determinations on coal and eight on associated materials was reported, and there were indications of a linear variation of thermal conductivity with ash content. For eight coals of 30 to 35 percent volatile matter and less than 10 percent ash, the reported values for thermal conductivity ranged from 0.00037 to 0.00055. A pyrite was reported at 0.0074.

Terres⁶¹ has reported the thermal conductivity of a single piece of coal of un-

identified kind as about 0.0006. The Fuel Research Board of Great Britain supplied Gilbert with a value equal to 0.00049 for bituminous coal, for use in his careful study of the mechanics of heat drying.⁶² There have also been some tests, under rather poorly controlled conditions, of heat conductance of coal in place underground.⁶³

Somewhat more work has been reported on aggregates. In 1928, Terres,⁶¹ using a method in which time-temperature curves are taken at two or more points in the direction of the flow of heat, reported that masses of closely sized coal grains ranging up to 5 millimeters had thermal conductivities of the order of 0.0003 to 0.0004 between temperatures of 25 and 130° C. Similar experiments with granulated coke at higher temperatures indicated that conductivity was linearly related to the temperature of test, the rate of increase being about 0.001 per 100-degree increase in test temperature. These latter tests ranged from about 180 to about 620° C, the values of thermal conductivity at the higher temperature being 0.002 and 0.003 for 1- and 2-millimeter particles, respectively.

Terres suggested that, during the progressive heating and transformation of coal into coke, the thermal conductivity increases without sharp break from approximately 0.0003 at 0° C to values at 1,000° C between 0.0027 and 0.0036, depending upon the type of coke produced. The highest values were associated with the densest cokes.

Later, Terres and his associates⁶⁴ used a calorimetric apparatus for the determination of the thermal conductivity of ag-

⁵⁸ Mayers, M. A., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 408-24 (1938).

⁵⁹ Smoluchowski, M., *Bull. intern. acad. sci. Cracovie*, **1910A**, 129-53 (1910). Aberdeen, J., and Laby, T. H., *Proc. Roy. Soc. (London)*, **113A**, 459-77 (1927). King, W. J., *Mech. Eng.*, **54**, 190-4, 275-9, 296, 347-53, 410-4, 492-7, 560-5 (1932).

⁶⁰ Sinnatt, F. S., and Macpherson, H., *Fuel*, **3**, 12-4 (1924).

⁶¹ Terres, E., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 657-84 (1928).

⁶² Gilbert, W., *Engineer*, **150**, 500-2, 530-2, 574-5, 587-9, 617-9, 640-2 (1930).

⁶³ Kolesnikov, P. T., *Podzemnaya Gazifikatsiya Ugli*, **1935**, No. 2, 9-11 (1935).

⁶⁴ Terres, E., Tjia, H. A., Herrmann, W., Johswich, F., Patscheke, G., Pfeiffer, J., and Schwarzmann, H., *Angew. Chem.*, **48**, 17-21 (1935).

PHYSICAL PROPERTIES OF COALS

gregates of particles of brown coal. For four sizes of particles, ranging up to 6 millimeters, with preheating temperatures of 150, 350, and 500° C, the thermal conductivities were explored at various ambient temperatures. For a preheating temperature of 500° C the thermal conductivities of the several grain sizes were found to rise with increasing ambient temperature and to be closely similar up to about 120° C. At 20° C they were about 0.00019, and at 120° C about 0.00025. Above 120° C, it was observed that minus 0.75-millimeter material gave a consistently lower value than 2- to 6-millimeter material, the respective values at 400° C being about 0.00039 and 0.00056.

These workers used and correlated their data with an expression for the effective thermal conductivity of an aggregate of particles. Their expression states, in the words of Mayers,⁶⁵ that "the effective thermal conductivity across any plane is equal to the average of the thermal conductivities of the air and fuel, weighted in proportion to the part of the plane covered by each, and the equivalent conductivity due to black-body radiation across the voids." By means of this equation, together with certain simplifying assumptions, Mayers was able to express the effective thermal conductivity of a fuel bed in terms of the true thermal conductivity of the fuel, the volume of voids and the temperature in the fuel bed, and the diameter of the largest particles. The thermal conductivity of the gas filling the voids is absorbed in a different part of his analysis and does not appear directly. As indicative of the order of magnitude yielded by his expression, the effective thermal conductivity of a fuel bed of coke at a temperature of 1,500° F and containing 50 percent void volume, with a fuel top size of 1 inch, was estimated to be

0.00414. Of the effective thermal conductivity so computed, the true conductivity of the fuel contributes so small a proportion (about 5 percent) that the effective conductivity of the bed is largely independent of the fuel used.

Theoretical aspects of this general problem have also received attention from Faggiani.⁶⁶

Burke, Schumann, and Parry⁶⁶ have presented evidence which indicates that laws of heat conductance hold for aggregates of crushed coal similar to those developed by Fourier in his classical treatment of the flow of heat through a homogeneous solid. In their analysis they neglected, however, the effect of radiation, which was later shown to be of considerable importance.^{68, 62} Their experimental work involved the subjection of a cylindrical mass of crushed material, initially at uniform temperature, to a constant higher wall temperature and the exploration of the temperature-time relationship at the axis of the cylinder by means of thermocouples. For two dried crushed coals and one dried crushed coke, excellent agreement was found with the shape of the curve as predicted by the Fourier analysis, and the results permitted the computation of thermal diffusivity, which is a measure of the rate at which a temperature wave travels⁶⁷ and is equivalent to the ratio of thermal conductivity to the product of specific heat and density. The thermal diffusivity of a 16-mesh Pittsburgh coal was 0.0094 square inch per minute in the range of 60 to 650° F at atmospheric pressure. If 0.3 is taken for specific heat and

⁶⁵ Faggiani, D., *Rend. ist. lombardo sci.*, **68**, 523-40 (1935).

⁶⁶ Burke, S. P., Schumann, T. E. W., and Parry, V. F., *Proc. Am. Gas Assoc.*, **12**, 820-55 (1930).

⁶⁷ Allen, H. S., and Maxwell, R. S., *A Textbook of Heat*, Macmillan & Co., London, 1939, p. 393.

unity for density, the thermal conductivity of this particular aggregate may be computed as 0.00030. For "monolithic" (coked and tested in place) coke, the thermal diffusivity was found to be 0.00367 square inch per minute in the range 60 to 1,000° F.

The effect of moisture on brown coal is to increase the thermal conductivity, according to work by Kegel and Matschak.⁶⁸ Particles about 2 millimeters in top size were studied in a circular two-plate apparatus, and the conductivities for conditions of 0, 15, 35, and 50 percent moisture were found to be 0.000181, 0.000208, 0.000320, and 0.000472, respectively.

Fritz and Diemke^{69, 70} have found the thermal conductivity of 32 coal samples (including anthracite) to lie between 0.000464 and 0.000864 at 30° C. The observed values seemed to be positively correlated with density, regardless of the source of sample. With increasing test temperature, the thermal conductivity of a cannel coal rose linearly from 0.000624 at 20° C, the rate of rise being of the order of 0.0000012 for each degree rise. Three coke samples gave widely varying results by the same method. An abstract only of this reference is available to the present writers, and it is not known definitely whether the method tests the thermal conductivity of the coal substance or of an aggregation of coal particles, although the latter appears more likely.

As a concluding paragraph to these remarks on thermal conductivity, attention is called to a report on the linear coefficient of thermal expansion of anthracite, made

by Myer.⁵⁸ For this work he prepared bars of solid anthracite 3 centimeters square and from 16 to 28 centimeters long and heated them slowly in a water bath over a 25 to 100° C temperature range. Observation of change of length was made with the aid of a beam of light reflected onto a scale by a mirror so arranged as to be deflected by expansion of the sample. Results on ten samples were reported, ranging from 0.021×10^{-4} to 0.049×10^{-4} centimeter per centimeter per degree Centigrade. In preparing the samples an attempt was made, though not always successfully, to cut them with the long axis parallel to the coal laminae. In the two samples yielding the highest values, the laminae were indistinct and irregular.

SPECIFIC HEAT

Specific heat may be defined as relative thermal capacity, referred to water at 15° C, or alternatively as thermal capacity per unit mass. The two definitions express identically the same thing.⁷¹ Specific heat is dimensionless, and units need not be assigned; however, the dimensionless units calories per gram per degree Centigrade or Btu per pound per degree Fahrenheit are frequently used.

As early as 1894, Landolt and Börnstein⁷² quoted figures of 0.2040 and 0.3145 for gas-coal. Other early data are given by Threlfall,⁷³ who, incidental to the main subject of his investigation on spontaneous heating, used the method of mixtures to obtain values in the range 0.35 to 0.45. He raised 1 or 2 pounds of minus 2-millimeter air-dried coal to 80° C, mixed it with a known quantity of water of a lower

⁶⁸ Kegel, K., and Matschak, H., *Feuerungstechn.*, **25**, 213-7 (1937).

⁶⁹ Fritz, W., and Diemke, H., *ibid.*, **27**, 129-36 (1939).

⁷⁰ Fritz, W., and Diemke, H., *Tech.-wirts. Ber. Reichkohlenkommissars*, **1941**, No. 2, 19 pp.; *Chem. Abs.*, **35**, 4939 (1941).

⁷¹ See p. 511 of ref. 67.

⁷² Landolt, H., and Börnstein, R., *Physikalisch-chemische Tabellen*, Springer, Berlin, 2nd ed., 1894, p. 129a.

⁷³ Threlfall, R., *J. Soc. Chem. Ind.*, **28**, 759-73 (1909).

ture, and noted the temperature rise of the water.

Perhaps the first extended investigation of the subject should be credited to Porter and Taylor,⁷⁴ who also used the method of mixtures after having tried Joule's method, which involves the addition by electrical means of a known quantity of heat to an insulated vessel containing a liquid and the substance to be tested. Joule's method was found to have an appreciably lower order of accuracy for coal than the method of mixtures. Porter and Taylor used coal sized between 0- and 20-mesh, heating it to the desired temperature and quickly transferring it into a quantity of water in a large calorimeter. Good reproducibility was attainable. A summary of certain of their data is presented in Table III, in which the effect of temperature on

metric fluid in their work with moisture-free coal, but this fluid was also shown, in a later paper,⁷⁵ to react exothermically with coal. The reaction of water with the dried Wyoming coal was observed to generate as much as 20 calories per gram in one test. The amount of heat so generated was studied for various coals at different total moisture contents. Fairly smooth curves were obtained, the generated heat approaching zero at what might be regarded as inherent moisture. This was particularly true of the Illinois coal.

It may be noted that the authors computed the specific heat of the water in coal^{74, 75} to be of the order of 0.85, which they interpreted to indicate that water is in part intimately combined with the coal, lending support to the colloidal theory of coal substance.

Work on graphite and on coke, by the

TABLE III
OBSERVED SPECIFIC HEATS OF CERTAIN AIR-DRIED COALS⁷⁴

Source of Sample	Proximate Analysis				Mean Specific Heat for Temperature Ranges of			
	Moisture	Volatile Matter	Fixed Carbon	Ash	28 to 65° C	25 to 130° C	25 to 177° C	25 to 227° C
	percent	percent	percent	percent				
West Virginia	1.8	20.4	72.4	5.4	0.261	0.288	0.301	0.314
Pennsylvania	1.2	34.5	58.4	5.9	0.286	0.308	0.320	0.332
Illinois	8.4	35.0	48.2	8.4	0.334 *			
Wyoming	11.0	38.6	40.2	10.2	0.350 *			

* As modified in a later publication.⁷⁵

Porter and Taylor pointed out the importance of moisture content on specific heat. They also called attention to and investigated the exothermic reaction of water on dry coal. Because of this reaction, they used toluene as the calori-

metric fluid in their work with moisture-free coal, but this fluid was also shown, in a later paper,⁷⁵ to react exothermically with coal. The reaction of water with the dried Wyoming coal was observed to generate as much as 20 calories per gram in one test. The amount of heat so generated was studied for various coals at different total moisture contents. Fairly smooth curves were obtained, the generated heat approaching zero at what might be regarded as inherent moisture. This was particularly true of the Illinois coal.

⁷⁴ Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper 113* (1916), 30 pp.

⁷⁴ Porter, H. C., and Taylor, G. B., *J. Ind. Eng. Chem.*, **5**, 289-93 (1913).

⁷⁵ Terres, E., and Schaller, A., *Gas- u. Wasser-fach*, **65**, 761-4, 780-4, 800-2, 818-21, 832-3 (1922).

furnace of special design. Provision was made for extremely rapid transfer of the material to the inner vessel of a water calorimeter, and, from the heating curve of the water, the mean specific heat was computed. Experimental technique was worked out with especial care. It was found that mean specific heat in the range 21 to $T^{\circ}\text{C}$, for any one coke or graphite, was well fitted by a cubic equation in T . Values for the range 21 to 400°C were 0.265, 0.259, and 0.253 for, respectively, a graphite, a coke containing 15 percent ash, and a coke containing 30 percent ash; for the range 21 to $1,300^{\circ}\text{C}$, the respective values were 0.403, 0.383, and 0.363. Further results of this investigation were reported in 1928.⁷⁷

Debrunner⁷⁸ studied five cokes intensively, following the experimental technique developed by Terres and Schaller⁷⁶ and verifying their conclusions.

In 1922, Briggs⁷⁹ presented a few data, ranging from 0.20 for an anthracite to 0.33 for a clarain. The work was done with a Bunsen ice calorimeter and freshly ground undried coal. Moisture contents were not reported.

The Bunsen ice calorimeter was also adopted by Coles⁸⁰ for use in his careful and systematic investigation, after he had surveyed the other possibilities. The Bunsen ice calorimeter utilizes the known change in specific volume of water passing from the solid to the liquid state at 0°C . A measurement of this change in volume for a known mass of water permits calculation of the quantity of heat absorbed.

⁷⁷ Terres, B., and Biederbeck, H., *ibid.*, **71**, 265-8, 297-303, 320-5, 338-45 (1928).

⁷⁸ Debrunner, P., *Dissertation, Eidgenössischen Technischen Hochschule (Zurich)*, **340** (1923), 31 pp.

⁷⁹ Briggs, H., *Trans. Inst. Mining Engrs. London*, **64**, 227-48 (1922).

⁸⁰ Coles, G., *J. Soc. Chem. Ind.*, **42**, 435-9T (1923).

Using 8 to 10 grams of minus 60-mesh coal, Coles noted a nearly linear variation of specific heat with moisture content, ranging for the coal reported from 0.252 at 1.48 percent water to 0.355 at 15.07 percent water. These and other data permitted the computation of the specific heat of the water content of coal, in all tests very close to 1.0. This may be compared with Porter and Ralston's value⁷⁵ of about 0.85, obtained by the method of mixtures. Further correction for the specific heat of "ash," found to be about 0.16 to 0.17, permitted the calculation of the specific heat of the coal substance. Values ranged from 0.21 for anthracite to 0.257 for cannel coal and were approximately inversely proportional to the ratio of carbon to hydrogen. This relationship may be useful for rapid estimates of specific heat.

In using Kopp's law for the calculation of specific heat from a knowledge of elemental constitution, agreement was good for fusain and anthracite and fair for bituminous coals.

Sinnatt and Macpherson⁸⁰ also investigated the specific heat of dry coals at about the same time, using the method of mixtures with alcohol as the calorimetric liquid. Their results ranged from 0.226 for a cannel coal to 0.252 for an Arley vitrain, in a temperature range of 25 to 40°C , approximately.

Gilbert⁸² used a value of 0.352, obtained by him for an English bituminous coal sized between $\frac{1}{2}$ and $\frac{3}{16}$ inch, in his study of heat drying. Pieters,⁸¹ following the method of mixtures, reported a value of 0.21 for a foundry coke and 0.28 for two low-volatile coals.

Myer⁵³ determined the cooling curves of twenty anthracites from 100 to 30°C , using minus 60-mesh material with as-re-

⁸¹ Pieters, H. A. J., *Het Gas*, **51**, 94-5 (1931).

ceived moisture content. From known thermodynamic properties of the cooling curve, the mean specific heat is readily obtainable. His twenty samples yielded results ranging from 0.195 to 0.324, although sixteen of the twenty were close to and averaged 0.267. No obvious correlation of specific heat with items of the proximate analysis presented itself. Tests of several different size fractions of one anthracite gave quite similar results. Individual samples of related materials gave the following values: Indiana bituminous coal, 0.326; graphite, 0.197; charcoal, 0.326; coke, 0.192.

Terres⁶⁴ and his coworkers, utilizing the essentials of Joule's method, determined the specific heats of several brown-coal chars to be consistently in the range of 0.333 to 0.345, although before carbonization the specific heats, as observed on a chart in their report, were much lower.

Fritz and Moser⁵² are reported to have conducted a series of tests on about forty German coals, although the method of test is not known. They found mean specific heat (c) in the range 24 to 100° C to increase linearly with volatile-matter content (V.M.) according to

$$c = 0.242(1 + 0.008 \text{ V.M.})$$

where volatile matter is expressed in percentage. They also developed an empirical expression relating the mean specific heat in the range 24 to $T^\circ\text{C}$ ($T < 250$) to T and to volatile-matter content. A further report with the same title has been made by Fritz and Diemke.⁵⁶

REACTIONS TO VISIBLE LIGHT

In recent petrographic studies, particularly those employing polarized light and polished coal surfaces, effort has been di-

rected toward measuring the degree of coalification and establishing a rank classification based on quantitative physical tests. The observed optical phenomena have also provided information for speculation on the nature of the decomposition and molecular rearrangement accompanying change in the rank of coal.

Index of Reflection. Hoffmann and Jenkner^{57, 58} used the Leitz slit microphotometer for measuring the index of reflection of vitrains over a wide range of coalification. This instrument consists essentially of a lamp stand, adjustable in height, a second stand with an adjustable slit shutter, and a microscope fitted with a photometer. A low-voltage lamp, equipped to give a diffused source of light, was used. The slit could be adjusted to different widths and heights and was equipped to hold filters.

The light passing the slit enters the photometer attached to the dark-field condenser and is resolved by a glass prism. One component beam, passed through a polarizer to the microscope, illuminates half the field of vision in the eyepiece by reflection from the specimen. The other component, which is reflected at an angle of 90 degrees, is employed for comparative purposes, passing through glass filters of various densities. An adjustable prism deflects the comparison beam through a right angle to pass through the polarizer and the analyzer; the beam is then deflected a third time through a right angle by the photometer cube. The circular field of the eyepiece is divided into two semicircular sections, one illuminated by the comparison beam and the other by reflection from the specimen. The intensity of illumination from the comparison beam is matched with that from the specimen by adjusting the

⁵² Fritz, W., and Moser, H., *Feuerungstech.*, **28**, 97-107 (1949).

⁵⁸ Jenkner, A., and Hoffmann, E., *Brennstoff-Chem.*, **13**, 181-7 (1932).

analyzer, and when the matching is complete, the position of the analyzer may be noted on a graduated scale. The percentage displacement of the reading on the scale from the position of zero intensity toward that of maximum intensity is accepted as a measure of reflected light and has been called the index of reflection. It is not to be confused with the reflection coefficient, which is the ratio of the light reflected from a surface to the total incident light.⁸⁴

Table IV gives the indexes of reflection measured with this apparatus on polished pieces of vitrain from several coals of various volatile-matter and ash contents. Neglecting ash content and regarding rank

TABLE IV

ASH, VOLATILE MATTER, AND INDEX OF REFLECTION OF COALS OF DIFFERENT RANK⁸⁷

No.	Colliery	Ash percent	Volatile Matter percent	Index of Reflection percent
1	Brassert	3.20	41.88	7.1
2	Scholler (Kladno)	2.00	37.33	7.3
3	Hannover	2.20	32.59	8.4
4	Prosper	1.45	26.27	9.0
5	Morgensonne	2.10	14.29	10.6
6	Gottfried Wilhelm	5.60	15.17	10.7
7	Ludwig	3.60	9.38	11.2
8	Langenbrahm	1.07	8.79	12.0
9	Marvine (Pennsylvania)	3.48	4.24	13.0
0	Trieben (Steiermark)	3.51	3.11	16.0

in a qualitative sense as inversely related to volatile-matter content, it will be observed that increase in rank was accompanied by increase in index of reflection for these ten coals, with one minor exception.

Similar conclusions were reached by Stach,⁸⁵ using a microscope with twin ob-

jectives for the simultaneous viewing of two specimens. In this apparatus, care must be taken that the intensity of illumination on the two specimens is exactly the same. Stach provided himself with polished sections of coal of known rank, as determined from the fuel ratio, and used them for comparison with unknown coals. When bituminous coal is to be examined, Stach suggested that the comparative observations be concentrated on vitrain bands, which were held to represent the nearest approach to pure and homogeneous coal, free from adventitious mineral matter.

Zhemchuzhnikov⁸⁶ has also discussed the increase of reflective power with increase of rank. In the second of these papers, he measured the luster of a number of Russian coals with a color analyzer and found that the degree of luster was inversely related to volatile-matter content, and that a luster-volatile matter curve on the basis of the observed data was useful for estimating the volatile-matter content from a luster-strength determination. A similar curve was constructed with data on coal from Donets coals.

Šimek and Ludmila⁸⁷ are reported to have made a careful study of several methods of measuring reflected light and of the influence thereon of such variables on particle size, ash content, petrographic analysis, and chemical treatment.

Index of Refraction. The index of refraction of any substance is defined as the ratio of the velocity of light in a standard medium to the velocity of light in the substance. It is also the ratio of the sine of

⁸⁴ *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, 23rd ed., 1939, p. 1900.

⁸⁵ Stach, E., *Glückauf*, **68**, 1029-32, 1052 (1932).

⁸⁶ Zhemchuzhnikov, Y. A., *Khim. Tverdogo Topliva*, **5**, 46-52 (1934); *Inst. Mekhanicheskoi Obrabotki Poleznuikh Iskopaemikh "Mekhanobr."* 15 yrs. *Socialistic Ind. Service*, **1**, 37-51 (1935); *Chem. Abs.*, **30**, 2727 (1936).

⁸⁷ Šimek, B. G., and Ludmila, J., *Hornický Vestník*, **18**, 297-301, 324-8, 353-5 (1936); *Chem. Abs.*, **32**, 1427 (1938).

the angle of incidence to that of the angle of refraction of a beam of light passing from a standard medium into the substance. The index of refraction of a substance varies slightly with the wave length of the refracted light and, in anisotropic substances, with the direction of the plane containing the incident and the refracted rays. For precise work a vacuum is used as the standard medium for the incident ray, but since the velocity of light in air is very little (about 0.03 percent) less than that in a vacuum, air is accepted as the standard medium in most petrographic work.⁵⁵

A number of methods, of varying degrees of accuracy and convenience, are available for the determination of the index of refraction.⁵⁶ One of these depends upon the fact that the reflected and refracted components of a ray of light falling upon a substance from a standard medium are each partially polarized, to an extent varying with the angle of incidence. That angle of incidence at which polarization is at a maximum is called the angle of polarization, and it may be shown that the tangent of the angle of polarization is equal to the index of refraction of the refracting substance.⁵⁷ The two terms may thus be used interchangeably, with proper regard for their arithmetic relationship, as expressions of the same physical property.

McCabe and Quirke^{58, 59} measured the angle of polarization of polished vitrains with a horizontal goniometer and a Leitz polarization apparatus. White light com-

ing through the signal slit and falling on the polished vitrain surface was almost completely polarized by reflection at a definite angle for each sample of vitrain, the refracted ray being absorbed. With the Nicol of the polarization apparatus set at right angles to the vibration direction of the light from the polished surface, it was possible, with relatively few trials, to determine when the angle of maximum extinction—that is, the angle of polarization—was reached. The rotating circle of the goniometer was so arranged that twice the angle of polarization was read directly, to an accuracy of about 15 minutes.

A number of vitrain samples were polished on three mutually perpendicular faces which made it possible to determine the angle of polarization in the different sections in which the coalified plant tissue was cut. In every instance the angle of polarization was identical for each of the directions of sectioning. The observations O_1 , O_2 , and O_3 , made on one specimen from No. 6 coal at West Frankfort, Ill. (Table V), are typical. Hence, it was assumed that orientation of the specimen with respect to the bedding of the coal was unnecessary.

To test the constancy of the angle of polarization throughout a single mine, several vitrain specimens from different parts of the mine at Nashville, Ill., were examined. The first five Nashville samples listed in Table V were collected for this purpose. Na_1 and Na_2 were from the same room, Nb_1 and Nb_2 were from a second room some distance from the first, and Nc was from a third room in still another part of the mine. The observed values of angle of polarization were identical.

A column collected from the Nashville mine in 1931 was also available for study.

⁵⁵ Johannsen, A., *Manual of Petrographic Methods*, McGraw-Hill Book Co., New York, 2nd Ed., 1915, p. 54.

⁵⁶ *Ibid.*, pp. 237–56.

⁵⁷ *Ibid.*, p. 58.

⁵⁸ McCabe, L. C., and Quirke, T. T., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 445–55 (1938). Quirke, T. T., and McCabe, L. C., *Bull. Geol. Soc. Am.*, **49**, 669–82 (1938).

TABLE V

ANGLES OF POLARIZATION, REFRACTIVE INDICES, AND PROXIMATE ANALYSES OF VITRAINS AND RELATED SUBSTANCES ^{55, 91}

Material	Source	Sample Number	Angle of Polarization ×2	Index of Refraction *	Proximate Analysis and Sulfur—As-Received Basis					Calorific Value	
					Moisture	Ash	Volatile Matter	Fixed Carbon	Total Sulfur	As Received	Moist Mineral-Matter-Free
					percent					Btu per pound	
Pleistocene lignitic wood	Fulton Co., Ill.		117° 00'	1.632							
Woody lignite	Hernando, Miss.	C-1697	117° 00'	1.632	32.1	3.8	32.9	31.2	0.59	6,765	7,048
Vitrain	Lafayette, Colo.	C-1048	119° 10'	1.703	21.7	2.4	29.5	46.4	0.26	9,997	10,265
Vitrain	Pershing, Iowa	C-1779	119° 30'	1.715	18.7	1.3	34.4	45.6	1.39	11,359	11,540
Vitrain	Middle Grove, Ill.	C-1703	119° 45'	1.723	16.0	0.7	33.6	49.7	1.60	12,075	12,188
Vitrain	Roanoke, Ill.	C-1704	119° 45'	1.723	15.7	1.2	33.5	49.6	1.19	12,123	12,303
Vitrain	Nashville, Ill.	Na ₁	120° 15'	1.741							
Vitrain	Nashville, Ill.	Na ₂	120° 15'	1.741							
Vitrain	Nashville, Ill.	Nb ₁	120° 15'	1.741							
Vitrain	Nashville, Ill.	Nb ₂	120° 15'	1.741							
Vitrain	Nashville, Ill.	Nc	120° 15'	1.741							
Vitrain	Nashville, Ill.	N18-2	120° 15'	1.741							
Vitrain	Nashville, Ill.	N18-5	120° 00'	1.732							
Vitrain	Nashville, Ill.	N18-7	120° 00'	1.732							
Vitrain	Nashville, Ill.	N18-29	120° 15'	1.741							
Vitrain	Nashville, Ill.	N18-47	120° 00'	1.732							
Vitrain	Nashville, Ill.	N18-51	120° 15'	1.741							
Vitrain	Nashville, Ill.	N18-57	120° 15'	1.741							
Vitrain	Nashville, Ill.	N18-76	120° 15'	1.741							
Vitrain	Bonneville, Ind.	C-1690	120° 30'	1.750	7.2	0.7	41.5	50.6	1.83	13,247	13,396
Vitrain	W. Frankfort, Ill.	O ₁	120° 45'	1.759							
Vitrain	W. Frankfort, Ill.	O ₂	120° 45'	1.759							
Vitrain	W. Frankfort, Ill.	O ₃	120° 45'	1.759							
Vitrain	Harrisburg, Ill.	C-1692	121° 00'	1.768	4.5	1.6	34.9	59.0	1.39	13,782	14,063
Vitrain	Gibsonia, Ill.	C-1691	121° 30'	1.786	2.3	1.7	40.1	55.9	1.91	14,438	14,769
Vitrain	Hartshorne, Okla.	C-1698	121° 45'	1.795	0.6	2.2	23.9	73.3	0.65	15,277	15,680

* Index of refraction = tangent of the angle of polarization.

This column had been sawed into 2-centimeter blocks parallel to the bedding from the bottom to top of the bed. Numbering from 1 at the underclay, there were 85 of these 2-centimeter blocks. Eight of these (N18-2, -5, -7, -29, -47, -51, -57, and -76, Table V), having good vitrain bands, were selected from the column for the determination of their refractive indices. In five of the blocks, the index of refraction was

found to be identical with that observed on fresh vitrains collected six years later, and in three it was lower, but still within the error of observation. The general similarity of index of refraction of the vitrain bands throughout the coal bed was indicated.

The excellent correlation of index of refraction with moist mineral-matter-free calorific value is shown by Fig. 2.

Horn⁹² and Fisher⁹³ have also noticed that the index of refraction increases with rank. A similar conclusion was reached by Hummel,⁹⁴ using the immersion method with liquids having refractive indices ranging from 1.571 to 1.728, in the examination

⁹² Horn, G., *Norsk Geol. Tids.*, **10**, 490 (1929); *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 453-4 (1938).

⁹³ Fisher, D. J., *Proc. Geol. Soc. Am.*, **1933**, 444-5.

⁹⁴ Hummel, K., *Z. deut. geol. Ges.*, **82**, 459-97 (1930).

of twenty samples, including peat, lignite, cannel, brown coal, and bituminous coal. The lowest index of refraction was noted for a peat; the highest for a low-volatile coal from the Donets district. No analytical data were reported.

Anisotropism. Distinct anisotropic effects under polarized light have been noted,^{37, 95} increasing in prominence roughly with increasing rank. The anisotropism of anthracite approaches that of graphite and is particularly evident in the

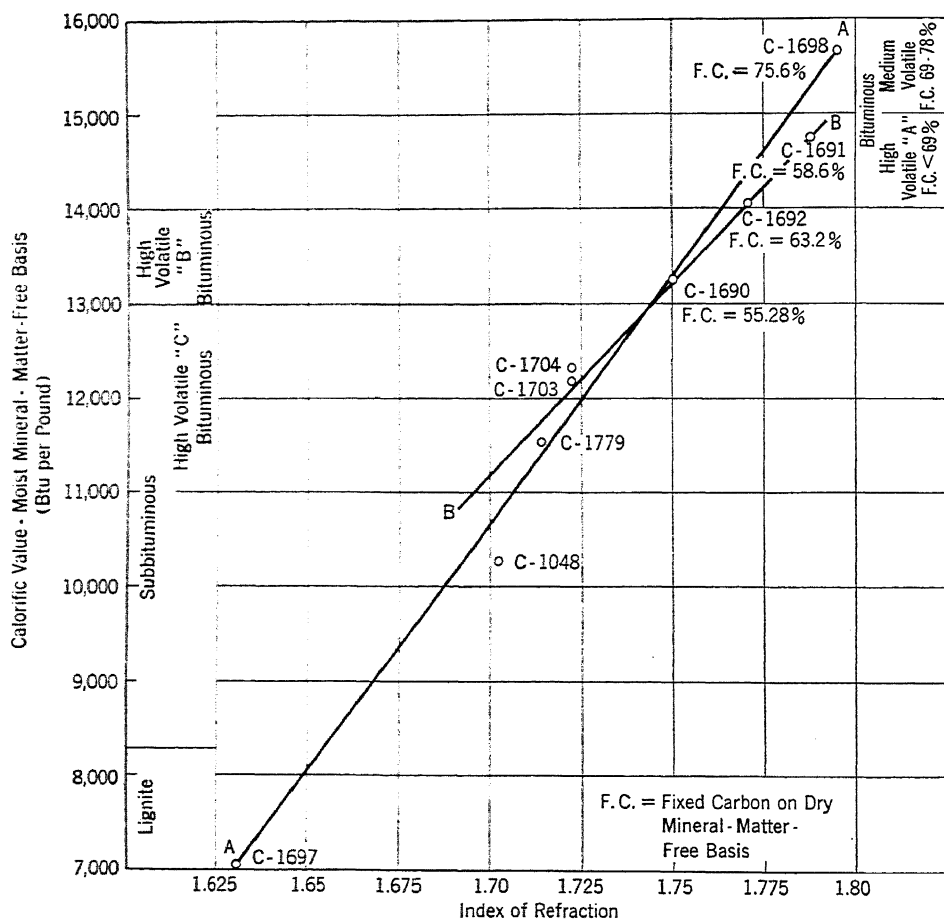


FIG. 2. Relationship of moist, mineral-matter-free calorific value to index of refraction of selected vitrains.⁹⁴

gellike substance of the coal.^{95, 96} The fusainized substance⁹⁵ and fusain from bituminous coal⁹⁷ exhibit no appreciable anisotropy.

EXAMINATION BY X-RADIATION

X-rays have been found to be useful in the endeavor to extend the knowledge of the mode of origin and the structural characteristics of coal. The uses of X-rays may be grouped into the two broad categories of absorption and diffraction methods.

X-Ray Absorption. X-ray absorption methods, or radiography, depend upon the fact that a beam of X-rays impinging upon a substance is differentially absorbed in a manner related to the atomic numbers of the elements encountered. For a given wave length of X-radiation, the mass absorption coefficient—that is, the fractional decrease in intensity for a beam of unit cross section per unit mass of material—is far greater for an absorbing substance of high atomic number than for one of low atomic number. A number of empirical expressions relating these variables have been developed, with varying degrees of theoretical adequacy but without complete satisfaction.⁹⁷ It is evident that the pure coal substance, composed of elements of relatively low atomic numbers, is far more easily penetrated than any mineral matter commonly found in it. After a beam of X-rays has passed through a substance to be examined, its point-to-point intensity may be analyzed in one of several ways.

The first radiographic examinations of coal were made at the Mines Hospital near

Saarbrücken in 1897, only two years after the discovery of what are now known as X-rays was announced by Röntgen. In succeeding years the possibility of radiographic methods received only occasional attention^{98, 99} until it attracted the interest of an English worker, C. Norman Kemp, who enthusiastically advanced the technique of radiography and contributed numerous articles to the literature,^{100, 101, 102, 103, 104, 105} reviewing early work and presenting original investigations.

A valuable survey of the uses to which X-radiation may be put in the study of coal, touching on both radiography and X-ray diffraction methods, was also given by St. John.¹⁰⁶

Fluorescent screens may be used to register the partially absorbed X-ray beam after it has passed through the substance under examination. Such screen images of coal specimens permit a rapid qualitative study of the coal while the specimen is being manipulated.¹⁰⁴ This technique is an adaptation of one widely used in diagnos-

⁹⁸ Couriot, H., *Bull. soc. ind. minérale*, **12**, 713-26 (1898). Daniel, J., *Ann. mines Belg.*, **4**, 3-16 (1899). Garrett, F. C., and Burton, R. C., *Trans. Inst. Mining Engrs. London*, **43**, 295-303 (1912). Iwasaki, C., *Tech. Repts. Tôhoku Imp. Univ.*, **1**, 101-35 (1920), **2**, 235-75 (1921), **4**, 159-61 (1924).

⁹⁹ Briggs, H., *Proc. S. Wales Inst. Engrs.*, **39**, 403-65 (1923).

¹⁰⁰ Kemp, C. N., *Trans. Inst. Mining Engrs. London*, **67**, 59-83 (1924).

¹⁰¹ Kemp, C. N., *J. Soc. Chem. Ind.*, **43**, 234-5T (1924).

¹⁰² McLaren, W., Kemp, C. N., and Tholason, J. L., *Trans. Inst. Mining Engrs. London*, **69**, 315-38 (1925).

¹⁰³ Kemp, C. N., *Proc. S. Wales Inst. Engrs.*, **42**, 411-37 (1926); *J. Roy. Soc. Arts*, **75**, 714-36 (1929).

¹⁰⁴ Kemp, C. N., *Proc. Roy. Soc. Edinburgh*, **48**, 167-79 (1928).

¹⁰⁵ Kemp, C. N., *Trans. Inst. Mining Engrs. London*, **77**, 175-85 (1929).

¹⁰⁶ St. John, A., *Trans. Am. Inst. Mining Met. Engrs.*, **74**, 640-53 (1926); *Coal Age*, **30**, 564-8 (1926).

⁹⁵ Sarbeeva, L. I., *Khim. Tverdogo Topliva*, **7**, 455-66 (1936).

⁹⁶ Zhemchuzhnikov, Y. A., *ibid.*, **7**, 467-8 (1936).

⁹⁷ Compton, A. H., and Allison, S. K., *X-rays in Theory and Experiment*, D. Van Nostrand Co., New York, 1935, pp. 533-55.

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tic medicine, but it has been little applied to the study of coal.

A more satisfactory method is to register the X-rays on photographic film. Kemp cut sections of coal $\frac{1}{2}$ inch in thickness normal to the bedding and prepared radio-

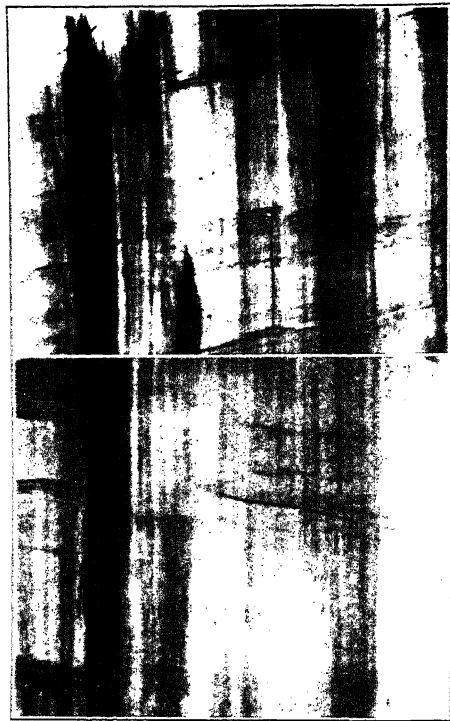


FIG. 3. Radiographs of halves of block of coal.¹⁰⁷

graphs by placing the face of the section in contact with the paper wrapping of the film. The rays were made to fall normal to the surface of the coal and after passing through were registered on the film (Fig. 3). Turner and Anderson¹⁰⁷ used the same procedure in their studies of anthracite, but in order that the mineral distri-

bution would be revealed more clearly, the sections were reduced to 1 millimeter in thickness.

As the X-ray photograph gives a denser positive image for refuse than for coal, it has been used in the laboratory to judge the effectiveness of the jigging operation.^{102, 103, 108} The relative proportions by volume of coal and refuse may be determined from the photograph, and, with the assumption of appropriate densities for coal and for refuse, the distribution according to weight can be estimated. Only in special cases does this method appear to have advantage over float-and-sink tests.¹⁰⁹

Some study has been given to coal-shale mixtures of varying known proportions to learn whether or not the relative amounts could be determined quantitatively by measuring the variations in intensity of a constant pencil of X-rays after passing through the samples. Variations in intensity of the emergent rays may be measured by directing the rays on a charged gold-leaf electroscope in a suitable metal chamber, and noting the rate of discharge of the leaf due to ionization of the air.^{100, 110} Kemp also experimented with comparison-type density meters to compare the opacity of photographic negatives with appropriate standards, but he had best success using microphotometric methods to measure variations of intensity on the photographic film.¹⁰⁵

Winter¹¹⁰ concluded that, if accurate quantitative determination is required, it is necessary to take into account the chemical composition of the ash. These investigators recommended the use of X-ray

¹⁰⁸ Mitchell, D. R., *Univ. Illinois Eng. Exp. Sta., Bull.* **258** (1933), 44 pp.

¹⁰⁹ Chapman, W. R., and Mott, R. A., *The Cleaning of Coal*, Chapman and Hall, London, 1928, p. 49.

¹¹⁰ Winter, H., *Glückauf*, **67**, 1105-11 (1931). Robertson, J. K., *Radiology Physics*, D. Van Nostrand Co., New York, 1941, p. 96.

¹⁰⁷ Turner, H. G., and Anderson, H. V., *Ind. Eng. Chem., Ind. Ed.*, **23**, 811-5 (1931); *Fuel*, **11**, 262-6 (1932).

absorption methods for rapid determination of the efficiency of coke- and coal-cleaning processes.

It should be noted that the minerals associated with the coal are not all equally impervious to radiation. Pyrite and calcite are more opaque than kaolinite and quartz, but the random orientation of the minerals makes difficult any attempt to determine ash accurately from a survey of the film. Whereas the coal substance is comparatively translucent, durain appears more opaque than its ash content warrants.¹⁰⁴ It may be concluded that the ordinary radiograph is most useful in the examination of the disposition of mineral matter in the coal lump and in obtaining evidence of the mode of deposition of adventitious mineral matter.^{99, 111}

From radiographs of slices of coal soaked in aqueous solutions of lead salts, Beeching¹¹² studied the nature of the porosity in several types of coal. Under the conditions of the experiment, dull coals were penetrated by the solutions, but bright coals were not. Fusain was usually more porous than durain. The greatest observed penetration of the lead solution was in a durain of high ash content. Calculations based on the rate of diffusion of the solution through Scottish splint indicated a mean diameter of capillaries of the order of 50 microns. Generally similar results were reported by Sinnatt,¹¹³ except that he would judge 50 microns to be approximately the upper limit of capillary diameter. It should be noted that further work by Sinnatt in the sorption of water vapor by coal gave results consistent with the hy-

pothesis of a gel permeated with capillaries of the order of 2 to 4 microns in diameter.

By means of stereoradiography, specimens may be viewed or photographed in a stereoscopic relief and structural features may be studied in detail, in their true three-dimensional relationship.¹⁰⁴ The appearance of a block of coal becomes something like that of a dirty block of ice,¹⁰¹ and the relative size, position, and nature of all mineral inclusions are brought into prominence. This technique has also been used in a study of the distribution of impurities in commercial coal of small size.¹⁰² Wilson¹¹⁴ has described the procedure in detail and has discussed the use of stereoradiographs to indicate the probable manner of fracture of coal due to subsequent mechanical handling.

X-Ray Diffraction. X-ray diffraction methods depend upon the fact that when a beam of collimated X-rays is allowed to penetrate a substance, under proper conditions, the beam is differentially diffracted in a manner characteristic of the substance. The diffracted beam may be registered on a photographic film placed a known distance and in a known manner from the substance. As is well known, the diffraction pattern of a single crystal so obtained is a number of "Laue spots," that of a randomly oriented aggregate of small crystal grains is a series of uniform concentric rings of characteristic intensity, and that of amorphous or colloidal substances is a series of broad diffuse halos. Preferred orientation of grains, molecules, or aggregations of atoms is indicated by maxima of intensity on the concentric halos.

Von Laue and the Braggs had first developed diffraction methods for use only with individual crystals of appreciable size,

¹¹¹ Briggs, H., *Trans. Inst. Mining Engrs. London*, **77**, 5-10 (1929); *Colliery Guardian*, **138**, 638-40 (1929). Forrester, C., *J. Inst. Fuel*, **9**, 30-58 (1935).

¹¹² Beeching, R., *ibid.*, **11**, 240-2 (1938), **12**, 35-9 (1938).

¹¹³ Sinnatt, F. S., *Fuel*, **19**, 5-7, 38-42 (1940).

¹¹⁴ Wilson, A. N., *J. Inst. Fuel*, **3**, 218-24, 342-6, 433 (1930), **4**, 64-5 (1930).

until Debye and Scherrer and Hull,¹¹⁵ independently and practically concurrently, introduced the essentials of the "powder" method, which permits the analysis of aggregates of submicroscopic crystals or groups of atoms. This method involves a narrow beam of monochromatic X-rays passed through a disordered mass of small particles of the substance under investigation. Disorder is essential, for the theoretical development of the method assumes perfect randomness of orientation. It is usually attained by fine pulverization and continuous rotation of the sample, which may be conveniently handled in capillary glass tubing. When considerable diffraction of the X-ray beam is anticipated, the photographic film is usually placed in the arc of a circle around the sample in order to use a minimum of film. The relative intensity and position of the halos and rings, when properly corrected and analyzed, permit an interpretation of the mean size of the ultimate particles or "crystallites" and of the atomic structure, as has been rigorously shown by von Laue.¹¹⁶ The theory underlying size determination from the broadening of the rings has been critically examined by Cameron and Patterson and by Jones.¹¹⁷ Jones suggested the admixture of a known crystalline substance in the form of large (> 1 micron) particles to the unknown substance as an experimental refinement.

In coal, however, the state of disorder of the crystallites is high, and the size of the crystallites is so small that there is only a comparatively slight amount of diffraction

under any conditions. Hence, coal is commonly studied without pulverization or rotation, and a flat photographic plate is adequate to intercept the diffracted rays.

Mahadevan^{118, 119} was one of the first users of X-ray diffraction methods in the study of coal, working on both vitrain and durain sections and on solvent extracts. His samples of vitrain, which he regarded as of homogeneous composition and structure, exhibited two diffuse halos which correspond to the most prominent rings of graphitic carbon. These have also been noted by McCabe (Fig. 4).⁵⁵ The positions of the two halos indicate diffracting particles of colloidal dimensions but no evidence of "free carbon."

Mahadevan gave particular attention to the scattering between the two halos, the intensity of which appeared to be related to the sum of moisture content and volatile-matter content for the vitrains observed. This suggested further work on dehydrating and devolatilizing the vitrains, which then yielded diffraction patterns with nearly clear interspaces. He interpreted this as indicating a stable residual carbon resembling graphite in molecular form, in intimate association with volatile matter and moisture, and involving a six-carbon ring of the well-known graphite type, each carbon atom being attached to another carbon atom. More recent investigations by Sedletskii¹²⁰ bear out this conclusion. Furthermore, the constancy of size of the diffracting particles, as indicated by the position of the halos, for vitrains of different moisture contents suggested that the

¹¹⁵ Debye, P., and Scherrer, P., *Physik. Z.*, **17**, 277-83 (1916). Hull, A. W., *Phys. Rev.*, **10**, 661-96 (1917).

¹¹⁶ Von Laue, M., *Z. Krist.*, **64**, 115-42 (1926).

¹¹⁷ Cameron, G. H., and Patterson, A. L., *Symposium on Radiography and X-ray Diffraction Methods*, Am. Soc. Testing Materials, 1936, pp. 324-38. Jones, F. W., *Proc. Roy. Soc. London*, **166A**, 16-43 (1938).

¹¹⁸ Mahadevan, C., *Indian J. Phys.*, **4**, 79-98 (1929); *Fuel*, **8**, 462-9 (1929).

¹¹⁹ Mahadevan, C., *Indian J. Phys.*, **4**, 457-66 (1930), **5**, 525-41 (1930); *Fuel*, **9**, 574-80 (1930), **14**, 231-42 (1935); *Quart. J. Geol., Mining Met. Soc. India*, **7**, No. 1, 1-24 (1935).

¹²⁰ Sedletskii, I. D., *Soviet Geol.*, **9** (6), 48-63 (1939); *Khim. Referat. Zhur.*, **1939**, No. 10, 96-7; *Chem. Abs.*, **34**, 6793 (1940).

presence of water is intermicellar rather than intermolecular.¹¹⁸

Mahadevan noted that the superposition of "ash" and graphite halos on a vitrain pattern gave a durain pattern, which appeared to be in accordance with the conclusions of Fermor¹³ on the nature of durain as reached by quite a different approach.

Distinct evidence has been presented by Turner and Anderson¹⁰⁷ indicating the similarity of the anthraxylon of anthracite to graphitic carbon in many but not all cases. These investigators obtained diffraction patterns very similar to those of cellulose. Calculations indicated that the number of carbon atoms making up the anthraxylon "particle" is about forty-eight. The examination of attritus from anthracite revealed no such fiber structure as was observed in anthraxylon except where the attritus contained many thin layers of anthraxylon. Sharp Debye-Scherrer rings, attributable to mineral matter, were evident in the attritus pattern.

Corriez,¹²¹ in examining "peranthracites" and "true" anthracites as designated by Lebeau,¹²² confirmed the similarity of the anthracite structure to the graphite lattice, concluding that the mean distance between the lattices of both types of anthracite is of the order of 3.6 angstrom units, or 3.6×10^{-8} centimeters, with a small but constant number of such lattices making up the crystallite. In lateral development, however, the types differed considerably, peranthracite possessing the larger size. Further work on the examination of low-ash bright coals has been done by Schoon,¹²³ using a microphotometer for the critical examination of the diffraction patterns, in

the manner suggested by Hofmann and Wilm.¹²⁴

Krishnamurti's¹²⁵ studies of amorphous carbon suggest that the average crystallite

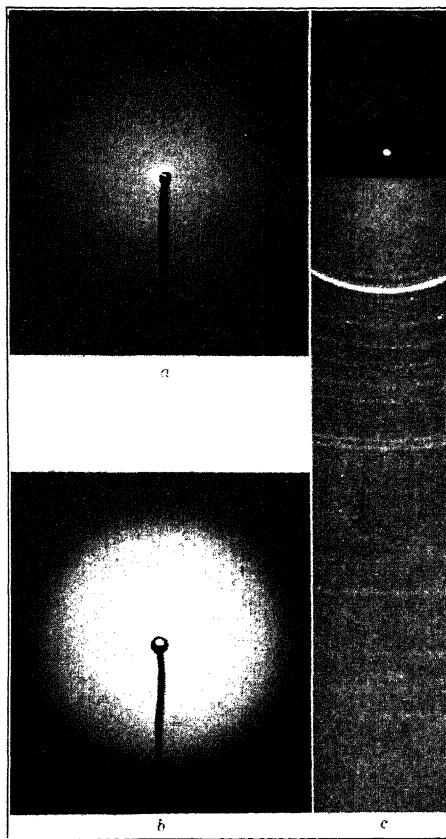


FIG. 4. X-ray diffraction patterns of (a) a lignite from Hernando, Miss.; (b) a vitrain from Harrisburg, Ill.; and (c) a graphite.⁵⁵

of this material resembles a somewhat distorted graphite lattice, about 3.83 angstrom units perpendicular to the layered lattices and about 177 square angstrom units in

¹²¹ Corriez, P., *Compt. rend.*, **199**, 410-2 (1934).

¹²² Lebeau, P., *ibid.*, **197**, 1234-6 (1933).

¹²³ Schoon, T., *Angew. Chem.*, **51**, 608-12 (1938).

¹²⁴ Hofmann, U., and Wilm, D., *Z. Elektrochem.*, **42**, 504-22 (1936).

¹²⁵ Krishnamurti, P., *Indian J. Phys.*, **5**, 473-88 (1930).

cross section parallel to the lattices, and contains about 60 carbon atoms.

In an important contribution Blayden, Riley, and Taylor¹²⁶ reported the dimensions of the graphite crystallites in cokes prepared under different conditions over the range 400 to 1,300° C, using finely pulverized material under conditions of very close experimental control and analyzing the patterns microphotometrically. In the coked product of the cellulose and the Northumberland coal they examined, carbon crystallites of graphitic type were evidenced, of a size for the coal of about 14 angstrom units perpendicular to the hexagonal planes and containing five such planes, and of 12 to 22 angstrom units parallel to the planes. The latter dimension varied markedly and regularly with the temperature at which the coal was carbonized.

Riley,¹²⁷ summarizing the diffraction method as applied to coal, has presented

¹²⁶ Blayden, H. E., Riley, H. L., and Taylor, A., *J. Chem. Soc.*, **1930**, 67-75.

¹²⁷ Riley, H. L., *Trans. Inst. Mining Engrs. London*, **95**, 48-61 (1935).

evidence to indicate that there are certain characteristics common to both coalification and carbonization, including the formation of small similar units of colloidal dimensions, consisting of large flat molecules arranged in a layered lattice. These units or crystallites are similar to graphite crystallites observed in certain forms of carbon, and it thus becomes important to have a clear picture of the graphite carbon lattice, in order that the advancement of knowledge may spread soundly from the known to the unknown. X-ray analysis shows that the graphite carbon lattice ideally consists of carbon atoms "arranged in flat planes and situated at the corners of regular vicinal hexagons. In the hexagon planes, the carbon atoms are each connected to three others by nonpolar valency bonds and are 1.42 Å units apart. The hexagon planes, which form a layered lattice, are 3.40 Å units apart and are held together by the metallic valencies which give graphite its electrical conductivity."¹²⁸

¹²⁸ Riley, H. L., *J. Inst. Fuel*, **10**, 149-56, 275-82 (1937).

CHAPTER 8

CHEMICAL CONSTITUTION OF COAL: AS DETERMINED BY HALOGENATION REACTIONS

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Deductions as to the chemical constitution of coal based on its reactions with halogens were made as early as 1881 when Bevan and Cross¹ reported that a cannel coal on treatment with aqueous chlorine solution was converted into a brown product which dissolved without residue in aqueous potassium hydroxide to a deep brown solution from which the product could be thrown out as a flocculent precipitate by neutralization with mineral acid. The product was similar to that obtained from lignified fibers and from cellulose sulfuric acid char by the action of aqueous chlorine solution, and the authors held it probable that "cellulose, lignin, peat, lignite, cannel coal, and anthracite are terms of a vast series of compounds differentiated under natural conditions." These same authors² also reported that treatment with dilute hydrochloric acid and potassium chlorate rendered the coal completely soluble in alkalies. They also found that the reducing action of all pseudo-carbons (presumably including coal) on sulfuric acid to produce sulfurous acid was inversely as the percentage of carbon and was completely absent from the pseudo-carbons after ig-

nition in chlorine. Smythe³ studied the products from the treatment of coal with dilute hydrochloric acid and potassium chlorate. An English bituminous coal and a German brown coal were rendered almost completely soluble in acetone by prolonged boiling in the reagent. The acetone-soluble product from the brown coal contained 22.93 percent chlorine. Less prolonged treatment of the bituminous coal gave a product which was soluble in acetone to the extent of 35 percent. Fractionation of the acetone-soluble material by means of benzene and alcohol extractions gave fractions, the compositions of which corresponded to empirical formulas as follows: benzene-soluble, $C_{30}H_{22}Cl_8O_{10}$; benzene-insoluble, alcohol-soluble, $C_{24}H_{15}Cl_4O_9$; and benzene-insoluble, alcohol-insoluble, $C_{22}H_{14}Cl_3O_5$ and $C_{25}H_{20}Cl_3O_8$. The compositions of these products indicate that the reaction is predominantly oxidation. The considerable work on the oxidizing action of hypohalites on coal is not included in the scope of this section.

In 1899, Ferd. Fischer⁴ cited some previously unpublished work of A. Stahlschmidt in which dry pulverized coal was

¹ Bevan, E. J., and Cross, C. F., *Chem. News*, **44**, 185-6 (1881).

² Cross, C. F., and Bevan, E. J., *Phil. Mag.*, **179**, 328-9 (1882).

³ Smythe, J. A., *Brit. Assoc. Advancement Sci. Rept.*, **1896**, 343-6.

⁴ Fischer, Ferd., *Z. anorg. Chem.*, **12**, 790 (1899).

reacted with dry bromine. After washing with alcohol and drying at 100 to 110° C the product contained 45.5 percent bromine. On the basis of analysis, it was concluded that most of the bromine had reacted by addition, only a small amount of hydrogen having been displaced. Boiling the product with sodium carbonate solution removed 0.7 percent of the bromine; ammonia solution removed 7.3 percent, and potassium hydroxide solution, 42 percent, respectively. Upon heating the product in a stream of carbon dioxide, evolution of hydrogen bromide began at 200° C; at 360°, 13 to 21 percent of the bromine was driven off according to the time of heating, whereas all bromine was driven off at red heat.

Hilpert, Keller, and Lepsius⁵ treated bituminous coal with bromine in the cold, on the water bath under reflux, in sealed tubes, and in acetic acid solution. In every instance the reaction product resembled the original coal in appearance, but gave off large amounts of hydrogen bromide on heating and yielded a noncaking residue.

Ferd. Fischer⁶ found that the oxidation of pyrite by bromine could not account for all bromine absorbed and concluded that coals contain varying quantities of unsaturated compounds, which add bromine, and compounds in which bromine substitutes for hydrogen. Iodine in alcohol reacted slowly with coal; chlorine in water reacted vigorously. Coal oxidized in air at 120–150° showed decreased ability to react with bromine, and coals that took up oxygen rapidly and tended toward spontaneous ignition also took up bromine readily.

Dennstedt and Bünz⁷ confirmed the ob-

servations of Ferd. Fischer in an investigation of the halogen absorption by coals of varying tendency toward spontaneous ignition in both the original and oxidized states. In Table I the coals are arranged in the order of increasing tendency to ignite spontaneously when heated in a stream of oxygen, the coal at the top of the list showing the least tendency to ignite.

TABLE I

HALOGEN ABSORPTION OF SOME COALS WITH DIFFERENT TENDENCIES TOWARD SPONTANEOUS COMBUSTION, BEFORE AND AFTER HEATING IN A STREAM OF OXYGEN⁷

Description of Coal	Oxygen Content	Milliequivalents of Halogen Consumed per Gram of Coal *
English bunker coal	4.02	1.19
oxidized	8.20	0.44
Westphalian bunker coal	2.62	1.62†
oxidized	15.17	0.83†
Durham steam coal	4.56	2.77
oxidized	18.99	1.43
Westphalian coal which ignited after 14 days in the bunkers of a ship	6.32	1.92
oxidized	19.10	1.17
English domestic coal	11.16	4.08
oxidized	21.41	1.55
Scottish steam coal	8.88	4.67
oxidized	21.23	1.77

* Determined by treating 1 gram of fine coal with 50 cubic centimeters of Hübl's reagent for 24 hours. Solution then made up to 100 cubic centimeters with 10 percent potassium iodide solution and a clear 50 cubic centimeter aliquot titrated.

† These values are transposed in the original reference. The author takes the responsibility of assuming a typographical error because of the consistency of other properties such as the Maumené number.

Other investigators have reported some results which are contradictory to those of Fischer and of Dennstedt and Bünz indicating that there are properties of coal affecting its tendency to ignite spontaneously, of which halogen absorption is not a criterion.

⁵ Hilpert, S., Keller, K., and Lepsius, R., *Ges. Abhandl. Kenntnis Kohle*, **1**, 25 (1917).

⁶ Fischer, Ferd., *Z. angew. Chem.*, **12**, 764–7, 759–80 (1899).

⁷ Dennstedt, M., and Bünz, R., *ibid.*, **21**,

Nübling and Wanner⁸ reported data on the bromine absorption and temperature of "ignition" of three coals and their pyridine extracts and residues (Table II). The Yorkshire and Ruhr coals were described as prone to spontaneous combustion, the Saar "Heinetz" coal as completely free

TABLE II

BROMINE ABSORPTIONS AND TEMPERATURES OF IGNITION OF SEVERAL COALS AND THEIR PYRIDINE EXTRACTS AND RESIDUES⁸

Coal or Fraction thereof	Milliequivalents of Bromine Absorbed per Gram of Substance	Temperature of "Ignition" °C
Yorkshire coal	1.5	138
Pyridine extract	0	146
Pyridine residue	3.25 (0.75?) *	173
Ruhr coal	1.75	152
Pyridine extract	0	146
Pyridine residue	4.75	187
Saar "Heinetz" coal	2.5	165-182
Pyridine extract	0	...
Pyridine residue	6.50	172

* These data were given at two points in the paper; once as 3.25 and once as 0.75. It was stated, however, that the pyridine residues showed greater bromine absorption than the original coals.

from the danger of self-ignition. The Saar "Heinetz" coal had the higher bromine absorption and higher ignition temperature. The pyridine extracts showed no bromine absorption whatever yet had ignition temperatures lower than the residues.

Hinden⁹ in reporting on observations of weathering in coal storage piles distinguished between coals not prone to oxidation, those undergoing oxidation without rise in temperature, and those given to spontaneous combustion. Five coals of the first type and one each of the other two types were characterized both by the amount of per-

manganate and by the amount of bromine reacting with the coal under given conditions (Table III). A finely ground 0.1-gram sample of coal was suspended in a solution of 10 cubic centimeters of concentrated sulfuric acid in 100 cubic centimeters of 0.1 *N* potassium permanganate at 70° C for 5 minutes, after which time the reaction was stopped by the addition of 100 cubic centimeters of 0.1 *N* oxalic acid solution and the excess oxalic acid titrated after filtering off the suspended coal. The reaction with bromine was measured by suspending 0.25 gram of finely ground coal in a solution of 100 cubic centimeters of 6 percent potassium bromide, 100 cubic centimeters of 0.01 *N* potassium bromate, and 20 cubic centimeters of dilute (1:1) sulfuric acid for 1.5 hours in a stoppered bottle shaken by a machine. The reaction was stopped by the addition of potassium iodide and excess reagent titrated after filtering off the suspended coal. The low bromine absorption of the samples from the coal which was found to have ignited spontaneously as compared to the bromine absorption of the five normal coals need not, however, be considered an exception to the findings of Dennstedt and Bünz. Hinden pointed out that there was no way of establishing whether the bromine absorption of the freshly mined coal was low or whether the low value was the result of absorption of atmospheric oxygen during the storage period. In the American coal whose bromine absorption after 4 years of storage still equaled that of the normal coals, the absorption for freshly mined coal should be considerably higher. Hinden's data show a parallel between halogen absorption and ability to react with oxidizing agents. Not much significance can be attached to this correlation because an aqueous halogen solution such as was used is an oxidation reagent. The markedly increased halogen

⁸ Nübling, R., and Wanner, H., *J. Gasbeleucht.*, **58**, 515-8 (1915).

⁹ Hinden, F., *Schweiz. Ver. Gas- u. Wasserfach.*, *Monats-Bull.* **4**, 417-23 (1924).

TABLE III

REACTION OF PERMANGANATE AND OF BROMINE WITH COALS SHOWING
DIFFERENT WEATHERING PROPERTIES ⁹

			Milliequivalents of Reagent Reacting per Gram of Coal (Ash-Free Basis)	
Description of Coal	Ash percent	Sulfur percent	Perman- ganat	Bromine
Coals showing normal resistance to weathering:				
Fairmont	9.4	0.85	50.8	17.0
Holmside	7.6	1.54	50.1	16.8
Saar-Stück (a)	5.1	48.9	16.2
Saar-Stück (b)	4.9	1.56	49.0	15.6
Saar-Nuss	3.9	0.70	47.1	16.0
American coal severely oxidized as the result of 4 years of storage without noticeable rise in temperature:				
a. Sample taken at 1 meter depth (no visible evidence of oxidation)	7.6	1.89	46.0	16.8
b. Highly oxidized sample from surface of the pile	35.0	2.57	64.4	19.4
English coal which ignited after 9 months' storage:				
a. Sample (bright surface) from cold part of pile	7.8	2.04	23.3	12.5
b. Sample (dull surface) from cold part of pile	4.4	1.14	35.7	9.2
c. Sample from hot 253° C. part of pile	29.0	2.37	37.9	17.4

absorption shown by a coal which had undergone severe atmospheric oxidation over that shown by the coal after limited atmospheric oxidation only is in contrast with the higher halogen absorption of freshly mined coal as compared to its absorption after limited atmospheric oxidation. This is probably due to the oxidizing nature of the halogenation reagent, the reaction being one of oxidation of products of a far-reaching degradation of the original coal.

Much of the published work relating to the reaction of coal with the halogens is devoted to the determination of the iodine number of various coals. The results of

these determinations depended more on the reagents and conditions used than on the types of coals studied. However, for a given technique, the estimated unsaturation or iodine number increased in general as the rank of the coal decreased. In Table IV are assembled the results of the various investigators; their techniques are described here briefly. Stahlschmidt ⁴ determined the bromine content of the coal after reaction with anhydrous bromine. Fischer ⁶ added successive increments of 0.5*N* potassium bromate solution to a suspension of coal in dilute hydrochloric acid until an excess of bromine persisted. Dennstedt and Bünz ⁷

TABLE IV

PUBLISHED VALUES FOR THE UNSATURATION OF COAL

Ref.	Reagent	Temp.	Time	Description of Coal	Milliequivalents of Halogen Consumed per Gram of Coal *	
4	Bromine (no solvent)	?	?	Bituminous	10.4	
6	Dilute HCl and <i>N</i> /2 KBrO ₃	Room	5 hr	Bituminous (4 varieties)	10 to 12.5	
				Semibituminous (3 varieties)	9	
				Anthracite	6	
7	I ₂ + HgCl ₂ in alcohol	Room	24 hr	Bituminous (3 varieties)	2.8 to 4.7	
				Semibituminous (3 varieties)	1.2 to 1.9	
8	Bromine in chloroform	Room	?	Bituminous (2 varieties)	1.5 to 1.7	
				Cannel	2.5	
9	Dilute H ₂ SO ₄ and <i>N</i> /100 KBrO ₃	Room	1½ hr	Bituminous (6 varieties)	9.2 to 17.0	
10	I ₂ + HgCl ₂ in alcohol	Room	2½ hr	Bituminous	2.02	
11	I ₂ + HgCl ₂ in alcohol + chloroform	Room	2½ hr	Bituminous (4 varieties)	1.9 to 2.5	
				Semibituminous	1.6	
12	<i>N</i> /10 iodine in KI solution	Room	24 hr	Components of banded coal:	Permanent	Temporary
				Vitrain	1.80	8.4
				Clarain	1.86	8.2
				Durain	1.40	7.0
				Fusain	0.34	0.17
	ICl in glacial acetic acid	Room	6 hr	Vitrain	5.35	1.46
				Clarain	4.98	1.64
				Durain	4.05	1.34
				Fusain	0.34	0.58
					By addition	By substitution
13	Bromine in CCl ₄	76° C	20 min	Bituminous	1.01	0.70
				Casseler Brown	0.87	0.65
14	ICl in glacial acetic acid	Room	15 days	Bituminous (9 varieties of Russian)	9.7 to 12.6	
				Semibituminous	9.0	
				Anthracite	1.2	
15	Br in CCl ₄	0° C		Bituminous	5.5	

* 2,000 milliequivalents of halogen consumed represent one double bond; that is, 2 milliequivalents of halogen consumed per gram of sample correspond to one double bond in a molecule of molecular weight of 1,000.

treated 1 gram of fine coal with 50 cubic centimeters of Hübl's reagent for 24 hours, then made the solution up to 100 cubic centimeters with 10 percent potassium iodide solution and titrated a clear 50 cubic centimeter aliquot. Nübling and Wanner⁸ added pure bromine dropwise to a suspension of powdered coal in chloroform until the solution stained filter paper yellow. Marcusson¹⁰ also used Hübl's reagent and titrated for excess reagent. When hydrochloric acid was added to Hübl's reagent

the iodine number was smaller. It was established that the lowering of the iodine number was caused by the competitive reaction of hydrochloric acid with the coal. Hart¹¹ allowed Hübl's reagent to react with a chloroform suspension of finely divided coal. In order to ascertain whether the bulk of the coal or only a soluble fraction was reacting, Hart determined the iodine number of the material extracted from coal by a mixture of chloroform and absolute alcohol corresponding to the mixture of chloroform and Hübl's reagent.

¹⁰ Marcusson, J., *Z. angew. Chem.*, **32**, 113-5 (1919).

¹¹ Hart, F., *Chem.-Ztg.*, **30**, 1204-5 (1906).

The 1 to 2 percent of extract so obtained had an iodine number about one-tenth that of the whole coal.

Stopes and Wheeler¹² determined the halogen absorption of the components of banded coal when treated with Wijs' solution and with iodine in potassium iodide solution. Although the absorption of halogen from Wijs' solution was several times as great as that from iodine in potassium iodide solution, with both reagents the reaction failed to reach a definite end point with respect to time. A distinction between "temporary" and "permanent" absorption was made. Apparently after titration of excess reagent the sample released iodine when allowed to stand. Vitrain, clarain, and durain showed about equal halogen absorption; fusain showed a much lower absorption.

None of the above investigators attempted to distinguish between halogen reacting by substitution and that reacting by addition. Fuchs,¹³ in studying the action of bromine on cellulose, lignin, brown coal, and bituminous coal, reacted dry powdered coal, previously freed of bitumen by extraction with a benzene-alcohol solution, with bromine in carbon tetrachloride solution by refluxing for 20 minutes. He determined the percentage of bromine in the reaction product and the amount of bromine removed as hydrogen bromide by boiling the reaction product with calcium acetate solution for 30 minutes; the latter he regarded as halogen introduced by addition reaction. The reaction product after treatment with calcium acetate would again absorb bromine which could, in turn, again be removed by treatment with calcium acetate. Fuchs found that bituminous coal, brown

coal, and lignin behaved similarly, in contrast to cellulose, which was unattacked by bromine.

Kusnetsov¹⁴ found that the absorption of iodine by coal depended, aside from the nature of the coal, upon the iodine reagent, upon the solvent, upon the excess of reagent, and upon the time of reaction. Thus, the absorption of iodine by 1 gram of dry finely powdered coal when suspended in 15 cubic centimeters of carbon tetrachloride and 25 cubic centimeters of Hübl's reagent (iodine and mercuric chloride in absolute alcohol) amounted to 1.11 milliequivalents after 1 day and 3.37 milliequivalents after 22 days. Under the same conditions, but replacing Hübl's reagent with Wijs' reagent (iodine in glacial acetic acid), the absorption of iodine was 0.92 milliequivalent after 1 hour, 2.14 milliequivalents after 20 hours, and 3.22 milliequivalents after 15 days. When the acetic acid in Wijs' reagent was replaced by carbon tetrachloride, the iodine absorption was 1.65 milliequivalents after 1 hour and 2.18 milliequivalents after 24 hours. When to the last solution were added, respectively, 0.5 gram and 0.1 gram instead of 1 gram of coal, the absorption after 24 hours amounted to 4.38 and 16.15 milliequivalents, respectively. By measuring the hydrogen iodide in the solution after reaction the amount of iodine used in substitution was determined. Substitution was least with Wijs' reagent and practically negligible at the shorter reaction times, but no data were given for the standard conditions chosen, namely, 0.1 gram of coal, 15 cubic centimeters of carbon tetrachloride, 25 cubic centimeters of Wijs' reagent, and 15 days' reaction time.

A quantitative determination of the halogen reacting with coal by addition and by substitution respectively under various con-

¹² Stopes, M., and Wheeler, R. V., *Fuel*, **2**, 83-4 (1923).

¹³ Fuchs, W., *Brennstoff-Chem.*, **9**, 348-50 (1928).

¹⁴ Kusnetsov, M. I., *J. Chim. Ukraine I, Tech. Part*, **1925**, 65-83.

ditions was carried out by Weiler,¹⁵ using bromine in carbon tetrachloride as reagent and employing an aeration technique¹⁶ which permitted excess bromine and any hydrogen bromide formed to be swept from the reaction vessel into a trap and then estimated by titration with thiosulfate, the bromine after addition of potassium iodide

but also a reaction in which hydrogen bromide is split out without the corresponding fixation of a bromine atom, the net result being the elimination of a hydrogen atom from the coal. This dehydrogenation effect was so marked at 65° C that considerably more bromine was evolved as hydrogen bromide than was fixed in the coal, with the

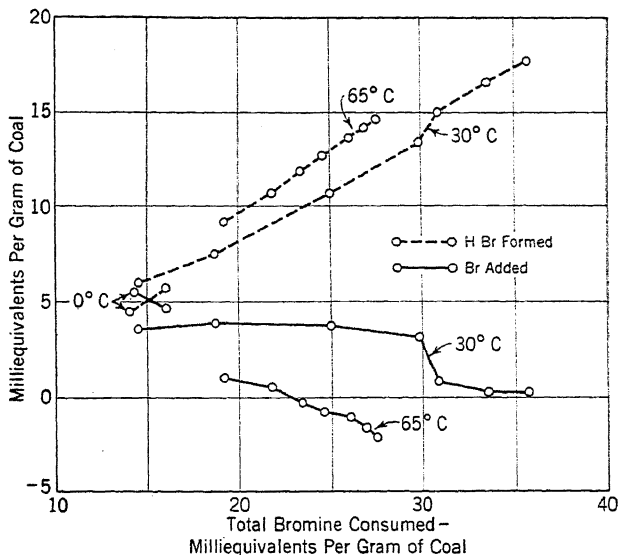


FIG. 1. Effect of temperature on hydrogen bromide formation and on apparent addition of bromine in the reaction of bromine in carbon tetrachloride solution on a coking coal.¹⁵

solution to the contents of the trap, and the hydrogen bromide after addition of potassium iodate solution following the first titration. The effects of time, temperature, concentration of reagent, and fineness of subdivision of the coal were evaluated in an effort to obtain a significant value for the unsaturation of the bituminous coal studied. It was shown that not only did the substitution and addition reactions of bromine with coal take place simultaneously even at temperatures as low as 0° C,

result that the calculated values for halogen reacting by addition were negative (cf. Fig. 1). The ease with which this elimination of hydrogen bromide occurred suggests that the elimination took place from hydroaromatic structures to form benzenoid compounds. Buckwalter and Wagner¹⁶ determined the unsaturation of some thirty compounds by the aeration method and found that negative values were obtained with only such compounds as contained aromatic or hydroaromatic (alicyclic) structures, e.g., menthane, retene, abietic acid, rosin, and heavy lubricating oil fractions. At 0° C, the elimination of hydrogen bro-

¹⁵ Weiler, J. F., *Fuel*, **14**, 190-6 (1935).

¹⁶ Buckwalter, H. M., and Wagner, E. C., *J. Am. Chem. Soc.*, **52**, 5241-54 (1930).

mide was largely suppressed and the figure of 5.5 milliequivalents of halogen reacting by addition per gram of coal was regarded as a satisfactory measure of the unsaturation. This estimated unsaturation means that two from every twenty-eight carbon atoms are linked to each other by olefinic double bonds.

The observations of Stahlschmidt⁴ and Fuchs¹⁸ that part of the bromine in brominated coal can be removed by treatment with boiling alkali solutions was confirmed by Weiler, who noted that approximately two-thirds of the bromine was thus removed as hydrogen bromide. This is probably the same sort of reaction as occurs spontaneously during the halogenation reaction. The residual bromine is most likely linked to aromatic structures present in the original coal or formed by dehydrogenation of hydroaromatic structures during the halogenation or during the alkali treatment.

McCulloch and his coworkers^{17, 18, 19, 20} studied the reaction of gaseous chlorine with powdered coal and investigated the properties of the reaction product. The reaction took place¹⁷ vigorously with the evolution of considerable heat, and the gaseous products contained large amounts of hydrogen chloride. The chlorine content of the reaction product was 24.4, 35.5, 36.0, and 35.4 percent for coals having a fixed carbon content of 90.6, 75.6, 71.0, and 61.3 percent, respectively.

If the yield of hydrogen chloride for twenty-nine varieties of coal when the re-

action was allowed to proceed at 70° C is plotted²⁰ against percentage of carbon of the coal on a pure-coal basis, a plot is obtained very similar to the one obtained by Seyler²¹ in classifying coals according to their carbon and hydrogen content on a pure-coal basis, the various classes of coals falling in similar positions in both plots. Some exceptions were noted; several coals of high pyrite content were found to yield much more hydrogen chloride than comparable coals of low pyrite content, the chlorination presumably having gone further as the result of catalysis.

Distillation of the chlorinated coal was accompanied by evolution of hydrogen chloride, no tar was formed, and the resulting residue was pulverous. Halogenation probably acts like oxidation to destroy tar yield and coking power. The volatile constituents which appear normally as tar and the fusible constituents responsible for coking undergo condensation reactions with elimination of hydrogen chloride or water at temperatures below those at which volatilization or fusion occurs, the result of the reactions being the production of nonvolatile and nonfusible products. For instance, Barash²² has shown that a mixture of a good coking coal with a sample of chlorinated coal will not coke at all despite the presence of agglutinants in the untreated coals. The evolution of hydrogen chloride commences below 200° C and continues in a regular manner until a temperature of 500 to 600° C is reached. At this temperature evolution practically ceases with the removal of most of the chlorine as hydrogen chloride. The same high-pyritic coals in which chlorination apparently proceeded further continued, however, to evolve con-

¹⁷ Marsh, A., McCulloch, A., and Parrish, E., *J. Soc. Chem. Ind.*, **48**, 167-74T (1929).

¹⁸ Eccles, A., and McCulloch, A., *ibid.*, **49**, 377-82T, 353-56T (1930). Eccles, A., Kay, H., and McCulloch, A., *ibid.*, **51**, 49-59T (1932). Kay, H., and McCulloch, A., *ibid.*, **51**, 186-90T (1932), **52**, 47-9 (1933).

¹⁹ Eccles, A., Kenyon, G. H., and McCulloch, A., *Fuel*, **10**, 4-15 (1931).

²⁰ Eccles, A., and McCulloch, A., *ibid.*, **10**, 308-19 (1931).

²¹ Seyler, C. A., *Fuel*, **3**, 15-26, 41-9, 79-83 (1924).

²² Barash, M., *J. Soc. Chem. Ind.*, **48**, 174-83T (1929).

siderable amounts of hydrogen chloride up to 900° C. If the coal (No. 3) of high pyrite content is excepted, Table V indicates that the percentage of the total hydrogen of the coal that is evolved as hydrogen chloride and water during chlorination and subsequent distillation of the chlorinated product decreased with increased rank and was proportional to the volatile matter determined in the original coal.

TABLE V

EVOLUTION OF HYDROGEN DURING CHLORINATION AND SUBSEQUENT DISTILLATION OF VARIOUS COALS¹⁹

Coal No.	1	2	3	4
Percent carbon in coal (dry, ash-free)	92.6	87.3	85.7	83.1
Volatile matter (dry, ash-free)	9.4	29.0	24.4	38.7
Percent of total H evolved as:				
(a) HCl and H ₂ O during chlorination	12.5	13.2	29.0	15.6
(b) HCl during distillation	27.0	33.1	41.2	33.2
(c) CH ₄ during distillation	10.4	11.9	5.2	11.4
(d) H ₂ during distillation	21.1	15.9	10.2	11.4
(e) H ₂ O during distillation over 200° C	5.6	8.4	4.8	14.1
(f) H remaining in coke above 900° C	23.4	17.5	9.6	14.3

The preparation of halogen acids by passing the gaseous halogen through a bed of brown coal, the reaction furnishing its own heat, has been described.²³ Nellensteyn²⁴ reported the formation of hydrogen iodide during the preparation of active carbon by the action of iodine on anthracite coal at 350° C.

²³ Reinau, *Z. angew. Chem.*, **39**, 557 (1926). Consolidierte Alkaliwerke, Ger. Pat. 313,875 (1918).

²⁴ Nellensteyn, F. J., *Chem. Weekblad*, **21**, 533-6 (1934).

Weiler²⁵ used exhaustive chlorination of coal to obtain an approximate measure of the apportionment of the carbon in coal between complex condensed ring structures on the one hand and aliphatic and simple cyclic structures on the other. By exhaustive chlorination of the coal using a hundredfold weight of antimony pentachloride at temperatures up to 400° C the aliphatic carbon and carbon in simple ring structures was driven off as the chlorinated hydrocarbons, C₆Cl₆, C₂Cl₆, and CCl₄, leaving the condensed ring systems as a highly chlorinated nonvolatile residue. In this manner it was estimated that 85 percent of the carbon of a bituminous coal from the Pittsburgh Seam is present in complex condensed ring structures. Additional unpublished work on coals of different ranks indicated that a lesser percentage of the carbon is present in complex ring structures as the rank of the coal decreases.

From this review of the reactions between coal and the halogens, it is concluded that a large portion of the carbon in coal is present in condensed ring systems. These ring systems are largely saturated, that is, naphthenic, and probably to a large extent hydroaromatic, that is, the rings are six-membered. Much of the hydrogen and of the lower hydrocarbons resulting from the carbonization of coal is the result of the dehydrogenation of these naphthenic structures to aromatic systems. Concerning the nature of the oxygen linkages little has been learned from halogenation reactions.

²⁵ Weiler, J. F., *J. Am. Chem. Soc.*, **58**, 1112-4 (1936).

CHEMICAL CONSTITUTION OF COAL: AS DETERMINED BY
OXIDATION REACTIONS

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Oxidation has been one of the most useful tools available to the chemist for establishing the structure of organic molecules. If the substance being investigated is of low molecular weight, identification of its oxidation products may lead immediately to a knowledge of its structure. With high-molecular-weight bodies, such as polymers, the results have been much less important. However, in oxidation studies of certain polymers, as, for example, the action of ozone on linear diene polymers, such as the natural and synthetic rubbers, where the regularly occurring double bonds offer a ready opening for attack, the results have been of the greatest significance.¹ The chemical and physical properties of bituminous coals indicate tridimensional or network structures, and hence a complicated series of oxidative degradation products is to be expected. Oxidation takes place, however, with convenient velocity with a number of oxidizing agents at a temperature such that there is little probability of internal structural changes, and even with these mild oxidation procedures some 80 percent of the carbon of typical American

bituminous coals can be recovered in the form of alkali-soluble substances. Because of the high yield of products of moderate molecular weight and the low temperatures required for reaction, oxidation has been used extensively for investigation of the structure of coals and related substances. Aside from the theoretical interest of these studies, the possibility of obtaining products of commercial value is always present, since an important part of the oxidation products consists of polycarboxylic acids, and acids of this type are finding wide application in the syntheses of resins and fibers.

STAGES OF OXIDATION

The oxidation of coals can, for convenience, be broadly divided into three stages.²

1. A surface oxidation, characterized by the addition of oxygen and the formation of oxygen-containing groups with acidic properties. With bituminous coals this reaction takes place with appreciable velocity at room temperatures and above. Carbon dioxide, carbon monoxide, and water may be formed concomitantly and are always liberated at higher temperatures or if the oxidation is prolonged. The rate

¹ Harries, C., *Untersuchungen über die natürlichen und künstlichen Kautschukarten*, Berlin, 1919, p. 17. Pummerer, R., Ebermayer, G., and Gerlach, K., *Ber.*, **64B**, 804-9 (1931). Hill, R., Lewis, J. R., and Simonsen, J. L., *Trans. Faraday Soc.*, **35**, 1067-89 (1939).

² Cf. Francis, W., *Fuel*, **17**, 363-72 (1938).

is a function of the rank of the coal as well as of temperature, oxygen partial pressure, and surface area. Superficially, the coal is little affected, at least in the early part of this stage, but it shows definite changes in caking and coking properties, heat of combustion, and susceptibility to further oxidation. The presence of acidic surface groups is indicated before any appreciable alkali solubility appears.

2. If oxidation is continued a large fraction of the organic material of the coal is converted ultimately into alkali-soluble, acid-insoluble products which have been designated "regenerated humic acids." In the freshly precipitated state they resemble hydrated ferric oxide, and they dry to shining black flakes, which on grinding form a reddish brown powder similar in appearance to finely ground coal. Transformation from stage 1 to stage 2 is accompanied by evolution of oxides of carbon and formation of greater or lesser amounts of lower-molecular-weight, soluble organic acids. These humic acids, "regenerated" by the oxidation of bituminous coal, are far from homogeneous, but they probably are of the same general type of structure, differing chiefly in molecular weight and the point of attachment of functional groups.

3. If the process which produced the humic acids of stage 2 is continued for a sufficient length of time or if more drastic oxidation methods are applied, the humic acids will be degraded completely to lower-molecular-weight acids soluble in acid and neutral, as well as alkaline, aqueous media. Transformation from stage 2 to stage 3, as in the previous step, is always accompanied by formation of carbon dioxide, until, if the oxidation is sufficiently prolonged, all the carbon appears in that form. The transformation to stage 3 is characterized by definite color changes, which are

presumably indicative of internal structural changes. The acids of stage 3, prepared from American bituminous coals, may furnish aqueous solutions ranging in color from the deep reddish brown characteristic of alkaline solutions of humic acids to a pale yellow. The intensity of color of these organic acids is a function of the extent of the oxidation and hence bears a definite relation to the fraction of the carbon appearing as carbon dioxide. With a Pittsburgh Seam bituminous coal, pale orange to yellow solutions are obtained when approximately 50 percent of the carbon of the coal has been converted to carbon dioxide, and colorless solutions are not obtained until upward of 90 percent of the carbon has been so converted, thus indicating the remarkable stability of the molecules containing these chromophoric groups. The nature of the color-bearing groups in the oxidation products of coal, although certainly of significance, appears to have attracted little attention. Such diverse oxidizing agents as nitric acid, alkaline permanganate, and molecular oxygen all furnish intensely yellow oxidation products. This yellow color is also present in the oxidation products from chars prepared by the pyrolysis of cellulose at moderate temperatures.

Although the greater part of the significant information concerning the nature of coal, obtained through oxidative degradation, has come from investigations of the simpler soluble acids formed in stage 3, certain facts of general interest are available from investigations of the earlier stages, and all will be discussed in the following paragraphs.

SURFACE OXIDATION

The initial step in the reaction of gaseous oxygen on coal, like that on activated car-

bons, appears to be one of addition with the formation of a surface complex.³ Simple reversible adsorption is ruled out because of the impossibility of recovering the oxygen except as oxides of carbon. Many workers⁴ have shown that coal, when exposed to an oxidizing atmosphere, reacts even at room temperature in such a way that some of the oxygen remains associated with the coal, while the balance appears as water, carbon dioxide, and carbon monoxide, the distribution of the oxygen among the reaction products being a function of the temperature of oxidation and of the coal used. (See also Chapter 18.) Francis and Wheeler⁵ have indicated the analogy between the reaction of oxygen with carbon, where a surface complex has been postulated and generally accepted, and its reaction with bituminous coal. In the reaction of oxygen with coal, however, the hydrogen-containing groups of the "ulmin molecule" are believed to play an important part in the formation of carboxyl groups which have no counterpart in the carbon-oxygen complex formed when carbon is oxidized.

There is some evidence that the reaction of oxygen with coal takes place by addition at double bonds.^{5, 6} Ferdinand Fischer⁶ pointed out that oxygen and bromine seem to act on coal in a similar manner, for certain coals which take on oxygen quickly and ignite spontaneously also react rapidly and consume relatively large amounts of

bromine. Döring⁷ and Habermann⁸ have confirmed Fischer's conclusions qualitatively. In agreement with such a mechanism is the postulation⁸ of peroxide formation. There appears to be little definite experimental evidence yet for the presence of peroxides on oxidized coal surfaces. Habermann⁸ was unable to get positive tests either with chromic acid and ether or titanous sulfate. An oxygen surface layer on an Illinois bituminous coal which is established very quickly and which oxidizes such a reagent as titanous chloride has, however, been found,⁹ and powdered coal, which has been exposed to the air, exerts a definite oxidizing potential when suspended in aqueous alkali around a platinum electrode.¹⁰ It is of interest to note in this connection that special forms of porous carbon have been developed¹¹ which activate oxygen sufficiently rapidly so that they can be employed as electrodes in galvanic cells without added cathodic depolarizers.

Samples of coals oxidized at moderate temperatures, when analyzed by the procedure of Ubaldini and Siniramed,¹² for determining carboxyl groups in humic acids, give results indicating the presence of such groups on the surface of oxidized coal. Increased adsorption of basic ions by an oxidized coal surface as compared with that of a fresh one may also be interpreted as indicating the development of acidic

³ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **1927**, 2958-67.

⁴ Bunte, K., and Brückner, H., *Angew. Chem.*, **47**, 84-6 (1934). Ref. 3, p. 2960. Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper* **65** (1914), 30 pp. Coles, G., and Graham, J. I., *Fuel*, **7**, 21-7 (1928).

⁵ Habermann, *J. Gasbeleucht.*, **49**, 419-22 (1906).

⁶ Fischer, F., *Z. angew. Chem.*, **12**, 764-7 (1899). Hart, F., *Chem.-Ztg.*, **30**, 1204-5 (1906).

⁷ T., *Fischer's Jahresberichte*, N. S., **39**, 13-5 (1908).

⁸ Cox, A. J., *8th Intern. Congr. Applied Chem.*, **10**, 109-28 (1912).

⁹ Yohe, G. R., and Harman, C. A., *J. Am. Chem. Soc.*, **63**, 555-6 (1941).

¹⁰ Unpublished data, Coal Research Lab., Carnegie Inst. Tech.

¹¹ Heise, G. W., and Schumacher, E. A., *Trans. Electrochem. Soc.*, **62**, 383-91 (1932).

¹² Ubaldini, I., and Siniramed, C., *Studi Ricerche Combustibili*, **4**, 333-45 (1932-33); *Ann. chim. applicata*, **22**, 340-52 (1932), **23**, 585-97 (1933).

groups.¹³ Similar indirect evidence is found in the fact that whereas the rates of oxidation of fresh and oxidized coal surfaces differ little in an alkaline oxidizing medium, where presumably the inhibiting layer of acidic oxidation products would be rapidly removed by solution, there is a marked difference in rate of oxidation in an acid medium.¹⁰ It has also been reported¹⁴ that auto-ignition temperatures are increased by surface oxidation.

An interesting feature in connection with surface oxidation of bituminous coals is the formation of carbon monoxide as one of the products even in oxidations at room temperature in the presence of excess oxygen. The temperatures at which it appears are too low to account for its formation by secondary decomposition of carbon dioxide, and there are few organic oxidations in which it would be expected as a primary product. Both ketone and ketene oxygen have been postulated¹⁵ as primary oxidation products of graphite surfaces and conceivably may be responsible for the carbon monoxide formed. Surface oxidation measurements on special fractions of bituminous coal have indicated that the residue from a benzene extraction absorbs at 60° C twice as much oxygen from air as the original coal,¹⁶ and that both residue and extracts oxidize more rapidly than the original coal. Work with the petrographic

constituents has shown¹⁷ that vitrain is the most, and fusain the least, easily oxidized in air at 100° C.

HUMIC ACIDS

Preparation and Purification. These oxidation products of bituminous coal, because of their solubility in aqueous alkali and other solvents, represent the least degraded oxidation product of coal to which it is possible to apply classical methods for characterization. They may be prepared from bituminous coals by alternate oxidation and alkaline extraction processes, as, for example: (1) by alternate exposure to air and extraction with a basic solvent;¹⁸ (2) by intermittent treatment with an acidic oxidizing agent such as nitric acid^{19, 20} or sulfuric acid²¹ and an alkaline extracting medium; or (3) by continuous treatment with an oxidizing agent in the presence of a basic solvent medium, as treatment with air in the presence of aqueous alkali or the use of alkaline permanganate.²² Electrolytic oxidation in aqueous alkali has also been used,²³ and recently extraction has been made with furfural.²⁴

The rate of formation of humic acids is a function of the rank of the coal as well as such other variables as temperature, oxidant, and so forth. The yield of humic acids as a function of time for four typi-

¹⁷ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **127**, 112-25 (1925). Tideswell, F. V., and Wheeler, R. V., *ibid.*, **127**, 125-32 (1925).

¹⁸ Morgan, G. T., and Jones, J. I., *J. Soc. Chem. Ind.*, **57**, 289-92 (1938).

¹⁹ Lilly, V. G., and Garland, C. E., *Fuel*, **11**, 392-400 (1932).

²⁰ Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **57**, 512-6 (1935).

²¹ Kreulen, D. J. W., *Brennstoff-Chem.*, **S**, 149-54 (1927).

²² Bone, W. A., Horton, L., and Ward, S. G., *Proc. Roy. Soc. (London)*, **127A**, 480-510 (1930).

²³ Lynch, C. S., and Collett, A. R., *Fuel*, **11**, 408-15 (1932).

²⁴ Fuchs, W., and Sandhoff, A. G., *Fuel*, **19**, 45-8, 69-72 (1940).

¹³ Vologdin, M. V., and Kamendrovskaya, E. A., *Khim. Tverdogo Topliva*, **7**, 22-3 (1936); *Chem. Abs.*, **33**, 6024 (1939). Vologdin, M. V., *Khim. Tverdogo Topliva*, **8**, 844-52 (1937); *Chem. Abs.*, **32**, 5186 (1938). Syskov, K. I., and Ushakova, A. A., *Khim. Tverdogo Topliva*, **8**, 692-702 (1937); *Chem. Abs.*, **33**, 1908 (1939). Radspinner, J. A., and Howard, H. C., *Ind. Eng. Chem.*, **15**, 566-70 (1943).

¹⁴ Peters, K., and Cremer, W., *Angew. Chem.*, **47**, 529-36 (1934).

¹⁵ Sihvonen, V., *Trans. Faraday Soc.*, **34**, 1062-74 (1938).

¹⁶ Davis, J. D., and Reynolds, D. A., *Fuel*, **5**, 405-11 (1926).

cal American bituminous coals, using 1 *N* nitric acid as oxidant, is shown in Fig. 1.²⁵ The yield from a given weight of coal rises to a maximum and then decreases owing to further oxidation of humic acid to the lower-molecular-weight soluble types. The effect of rank of coal on rate of formation is very marked, the maximum yield with

flotation and by hand-picking, from Herrin, Illinois No. 6 Seam, with air at 150° C, and found that the vitrain samples gave 95 to 96 percent conversions to alkali-soluble material; the clarain, 82 to 83 percent; and the durain, 59 to 63 percent. There is considerable evidence to indicate that fusain oxidizes much more slowly than

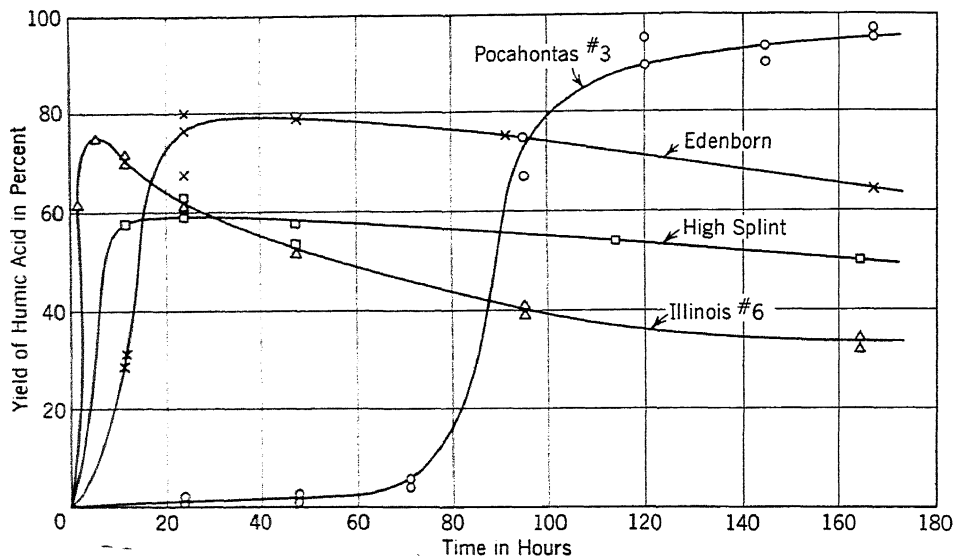


FIG. 1. Rate of humic acid formation from bituminous coals by 1 *N* nitric acid.²⁵

the low-rank Illinois coal being reached in about one-twentieth the time required for the high-rank Pocahontas coal because of the low rate displayed by the Pocahontas coal in the early stages. After this "induction period" there is little difference in rate.

The effect of the various petrographic constituents on rate of humic acid formation has been recently investigated by Yohe and Harman,²⁶ who oxidized samples of vitrain, durain, and clarain, separated by

other petrographic constituents, and this fact has been made the basis of a method for its quantitative determination.²⁷ The view that regenerated humic acids are derived exclusively from oxidation of "humins" or "ulmins" in the coal is not in accord with the fact that both the "bitumens" extracted from bituminous coal by benzene at elevated temperatures, and the part of the coal insoluble in benzene at elevated temperatures, yield "humic acids" on oxidation. Biggs²⁸ investigated "humic

²⁵ Lowry, H. H., *J. Inst. Fuel*, **10**, 291-301 (1937).

²⁶ Yohe, G. R., and Harman, C. A., *Trans. Illinois State Acad. Sci.*, **32**, No. 2, 134-6 (1939).

²⁷ Fuchs, W., Ganger, A. W., Hsiao, C. C., and Wright, C. C., *Penna. State Coll., Mineral Ind. Expt. Sta., Bull.* **23** (1938), 43 pp.

²⁸ Biggs, B. S., *J. Am. Chem. Soc.*, **58**, 1020-4 (1936).

acids" prepared from both materials and noted little difference in ultimate composition and equivalent and molecular weights. The data are shown in Table I.

appear to have been applied to the degradation products of coal.

Action of Solvents. The usual method of preparation of "regenerated humic acids"

TABLE I

PROPERTIES OF HUMIC ACIDS PREPARED FROM BENZENE-SOLUBLE AND -INSOLUBLE FRACTIONS OF PITTSBURGH SEAM COAL²⁸

Humic Acid from	Composition						Average Molecu- lar Weight	Average Equivalent Weight (Carboxyl)	Average Equivalent Weight (Car- boxyl and Hydroxyl)
	Carbon percent	Hydrogen percent	Nitrogen percent	Sulfur percent	Ash percent	Oxygen percent			
Extract A	60.95	4.19	3.76	0.48	0.76	29.86	193	240	181
Extract B	57.17	3.71	3.09	0.34	0.95	34.74	217	192	141
Residue	60.17	3.89	3.04	0.55	0.98	31.37	242	244	162

A and B represent fractions of the extract soluble and insoluble in ethyl ether, respectively.

It has already been indicated that the humic acids represent a series of molecules of an intermediate stage of complexity between the original coal substance and the simpler water-soluble acids. Insufficient work has yet been done on physical methods of fractionation to permit drawing conclusions as to distribution of molecular sizes. The usual method of purification has consisted in solution in alkali followed by precipitation with a mineral acid, but because of the flocculent nature of the humic acid precipitate considerable amounts of low-molecular-weight bodies both organic and inorganic may be occluded, and re-solution and reprecipitation may effect very little purification. Chloride ion, as well as some of the low-molecular-weight but difficultly soluble aromatic acids, i.e., iso- and terephthalic acids, appear to be very difficult to eliminate. Electrodialysis furnishes an ideal method for removal of electrolytes.^{29, 20} Methods of fractionation, by diffusion or centrifuging, which have yielded such important results with other colloidal systems do not as yet

depends upon solution in aqueous alkali and reprecipitation on acidification. Solubility in organic solvents appears to depend very largely on the extent and nature of the original degradation. As would be expected, basic organic compounds are often effective solvents, as are also phenolic compounds. Even after exhaustive methylation, and presumably complete conversion of the strongly polar carboxyl and hydroxyl groups to methoxyl, solubility in a solvent of moderate activity, like acetone, is often incomplete. Recently it has been found that the primary oxidation products of an Upper Freeport Seam bituminous coal are soluble in furfural. It was shown that the oxidation may be carried out either by a brief treatment with 16*N* nitric acid²⁴ at 100° C or by air oxidation followed by alkaline permanganate.³⁰ These furfural solutions were found to be optically void when examined in the dark field. The results of investigations of electrical and optical properties such as dielectric constant, conductivity, and light absorption were interpreted to indicate phenomena of both elec-

²⁹ Biesalsky, E., and Berger, W., *Braunkohle*, **23**, 197-201 (1924-5).

³⁰ Fuchs, W., and Fuchs, F., *Fuel*, **19**, 241 (1940).

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electrolytic dissociation and molecular association. A preliminary study of infrared spectra was stated to indicate that the association is probably not caused by either hydrogen or hydroxyl bonds. Refractive indexes could not be obtained at higher concentrations than 0.25 percent, owing to "anomalous dispersion." No significant difference was found between the surface tension of the furfural and a 2 percent solution of the "humic acids." Viscosity measurements were made on furfural solutions of both the free acids and methylated material. The deviations from the Einstein equation are of the same order as observed by Loughborough and Stamm³¹ for solutions of lignin.

Molecular and Equivalent Weights. Since the regenerated humic acids consist of a series of molecular sizes analogous to polymeric homologous series, molecular-weight determinations on any given sample can represent only an average value and the particular type of average will depend upon the method used.³² The average values obtained by colligative methods, such as freezing point, boiling point, and osmotic pressure, which yield number averages, are particularly sensitive to the presence of small weight percentages of low-molecular-weight species. Because of the difficulty of obtaining suitable solvents few data are available on the measurements of molecular weight of humic acids from any source. Odén³³ determined equivalent weights of humic acids extracted from peat, by electrometric titration, and estimated the molecular weight from the basicity, calculation of the basicity being made from the empirical conductance rule of Ost-

wald.³⁴ Odén concluded that it is very probable that this humic acid preparation was tri- or tetrabasic. Since an equivalent weight of approximately 340 had been found, this would lead to an estimated value of molecular weight for these acids of 1,000 to 1,350. Fuchs showed³⁵ that the natural humic acids of brown coal could be converted into products soluble in acetone by a brief treatment with 5 *N* nitric acid at 60° C. Determinations of the molecular weight of these products, by boiling-point elevation in acetone, led to an average value of 1,250. Thiessen and Engelder³⁶ determined the molecular weight of the alcohol-soluble fraction of humic acids extracted from decayed cedarwood by boiling-point elevation in acetone and obtained an average value of 800. Samec and Pirkmaier³⁷ made osmotic-pressure measurements on purified ammonium salts of humic acids extracted from brown coals and obtained values of 1,235 to 1,445. Smith and Howard³⁸ prepared humic acids by the action of 1 *N* nitric acid on Pittsburgh Seam bituminous coals. These acids were found to be soluble in dihydroxyphenols, such as catechol, and cryoscopic measurements in this solvent led to average values around 300.

The very considerable variations in average values of molecular weight reported may be ascribed in part to the molecularly heterogeneous nature of the materials under investigation and partly to peculiar specific molecular properties. Studies³⁸ on

³⁴ Ostwald, W., *Z. physik. Chem.*, **1**, 97-109 (1887).

³⁵ Fuchs, W., *Brennstoff-Chem.*, **9**, 178-82 (1928).

³⁶ Thiessen, G., and Engelder, C. J., *Ind. Eng. Chem.*, **22**, 1131-3 (1930).

³⁷ Samec, M., and Pirkmaier, B., *Kolloid-Z.*, **51**, 96-100 (1930).

³⁸ Howard, H. C., *J. Phys. Chem.*, **40**, 1103-12 (1936).

³¹ Loughborough, D. L., and Stamm, A. J., *J. Phys. Chem.*, **40**, 1113-32 (1936).

³² Lansing, W. D., and Kraemer, E. O., *J. Am. Chem. Soc.*, **57**, 1369-77 (1935).

³³ Odén, Sven, *Die Huminsäuren*, Theodor Steinkopff, Dresden, 1922, pp. 84-92.

other primary degradation products of coal such as the "bitumens" obtained by mild hydrogenation or pyrolytic breakdown, which are soluble in a number of organic solvents, show very great differences in apparent molecular weight depending upon the solvent employed. For example, the values for molecular weight for these degradation products in a strongly polar solvent like catechol may be as low as a fourth of those in a nonpolar solvent like diphenyl, and large variations in apparent molecular weight with change in concentration of solute have also been observed in the non-polar solvent. Both these facts point to association. It seems probable that we have to deal with similar phenomena with the humic acids.

Regardless of the exact value of molecular weight of the regenerated humic acids it is evident that the original coal structure degrades to relatively simple fragments with mild oxidation treatment.

Ultimate Composition. Ultimate composition being a rather insensitive property, it is perhaps not surprising that the carbon, hydrogen, and oxygen contents of "humic acids" from a variety of sources do not vary greatly. Typical data are shown in Table II. The acids prepared by Yohe and Harman²⁸ show higher carbon and lower hydrogen contents than those reported by other workers, probably owing to the mild degradation method employed.

The high carbon-hydrogen ratios point conclusively to condensed cyclic structures. Where complete analyses have been made, nitrogen and sulfur are always found and the nitrogen appears in greater amounts in those humic acids which have been prepared by the action of nitric acid. Evidence has been presented for the view that a part of the nitrogen in products resulting from the action of nitric acid on coal is

present as isonitroso groups.³⁹ An early worker⁴⁰ stated that part of the nitrogen was present as nitro groups.

A paper by Morgan and Jones¹⁸ is of particular interest in connection with the ultimate composition of regenerated humic acids. The acids in this study were prepared by oxidizing a sample of a British bright coal on shallow trays at 150° C, the coal layer being stirred each day. After about 8 weeks it was found that alkali solubility had reached a maximum, and the humic acids were extracted by 2 percent alkali and recovered and purified in the usual way. Further oxidation of these humic acids with alkaline permanganate, using a number of permanganate-humic acid ratios, led to the interesting observation that there was a gradual change in composition, as well as in the amount of humic acids recovered, up to a ratio of around 2.9. Above this ratio the amount of humic acids recovered continued to decrease, owing to conversion to soluble acids, but their composition was unchanged. The data are illustrated in Fig. 2. No figures were given on the yield.

Functional Groups. Relatively little work has been done on the determination of the functional groups in humic acids regenerated from bituminous coals. Like the natural acids, they undoubtedly contain carboxyl and hydroxyl groups. Electrometric titration with the hydrogen, quinhydrone, antimony, or glass electrodes has been used to determine carboxyl groups. An aqueous suspension of the acids, which has a pH of about 4, can be titrated directly with the standard alkali, but, since in a heterogeneous system of this kind at-

³⁹ Fuchs, W., *Die Chemie der Kohle*, Julius Springer, Berlin, 1931, pp. 201-2. Compare, however, ref. 29.

⁴⁰ Friswell, R. J., *J. Chem. Soc. (Proc., p. 9)*, 1892.

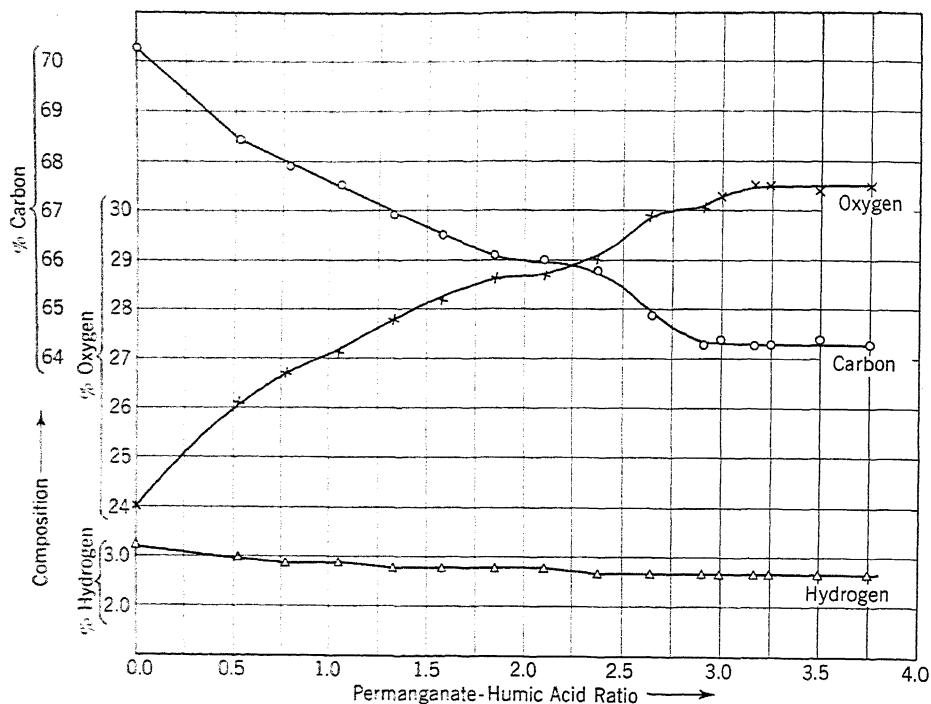


FIG. 2. Change in composition of humic acids by permanganate oxidation.¹⁸

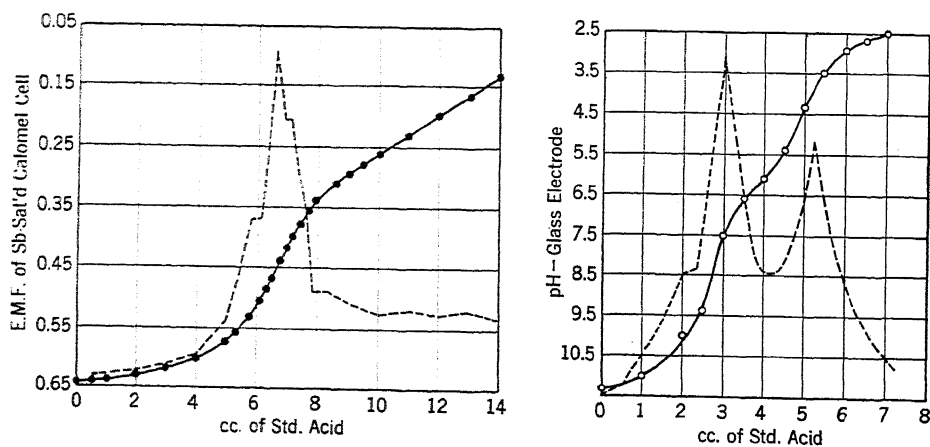


FIG. 3. Titration curves of humic acids.^{20, 41}

tainment of equilibrium is slow, it is preferable to dissolve the acids in an excess of standard alkali and to determine this excess by back titration.⁴¹ Typical curves for regenerated acids are shown in Fig. 3. Since we are dealing with rather weak acids it is desirable to plot a derived curve to locate the end point, and by this procedure

boxyl groups have been proposed by Ubal-dini and Siniramed.⁴² In one of these the humic acid is refluxed with a suspension of calcium carbonate in aqueous calcium acetate and the evolved carbon dioxide is weighed. Data on this method for one sample of humic acids and various known acids are shown in Table III.

TABLE II
ULTIMATE COMPOSITION OF HUMIC ACIDS FROM BITUMINOUS COALS

Method of Oxidation	Carbon percent	Hydrogen percent	Nitrogen percent	Sulfur percent	Ash percent	Oxygen percent
Hydrogen peroxide followed by alkali extraction (a) ⁴²	62.5	2.8	2.25
Alkaline permanganate ²²	56.7	3.35	1.2	0.6	38.1
Electrolytic, in alkaline me- dium ²³	57.6	5.0	3.1
1 N nitric acid, followed by alkali extraction ²⁰	60.7	3.1	2.7	0.9	28.9
Air at 150° followed by alka- line permanganate (b) ¹⁸	to 62.1	to 3.3	to 4.0	0.65	to 1.44	to 31.9
Air at 150° followed by al- kali extraction (c) ²⁶	64.3	2.7	1.6	0.9	30.5
16 N nitric acid, followed by extraction with furfural, followed by solution in alkali ²⁴	71.27	3.60	1.56	0.71	22.86
	60.1	3.2	5.9	0.4	30.4

(a) A limiting composition said to be the same for all coals examined.

(b) A "constant" composition obtained by exhaustive oxidation.

(c) From Illinois No. 6 vitrain, ash- and moisture-free basis.

the determination of neutral equivalent is a readily reproducible measurement. Duplicate determinations on the same preparation have been shown ²⁰ to agree within 2 percent.

In view of the behavior of known hydroxy aromatic acids, such as *o*-, *m*-, and *p*-hydroxybenzoic and β -resorcylic acids, there appears little doubt that the main inflection in the titration curve occurs when sufficient alkali is present to react with the carboxyl group alone.

Other procedures for determining car-

Formation of salts and determination of the amount of cation combined have also been employed ⁴² for determining the functional groups present in humic acids. Francis and Wheeler prepared barium, iron, silver, and copper salts and estimated the equivalent weight of their acids to be 170. Through reactions with acetyl chloride, benzoyl chloride, and Grignard reagents it was established that 860 grams was the weight of the unit associated with one hydroxyl group and that four carboxyls were present in this same unit.

⁴¹ Brown, C. F., and Collett, A. R., *Fuel*, **17**, 359 (1938).

⁴² Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **127**, 2236-45 (1925).

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TABLE III

EQUIVALENT WEIGHTS BY THE METHOD OF
UBALDINI AND SINIRAMED ²²

Acid	Theoretical Equivalent Weight	Found *
Benzoic †	122	122.7 123.1
Phthalic †	83.03	84.2 84.6
<i>o</i> -Hydroxybenzoic ‡	138	141.8 138.4
<i>p</i> -Hydroxybenzoic ‡	138	134.5 134.3
<i>m</i> -Hydroxybenzoic ‡	138	136.4 136.1
Succinic §	59	60.6 60.6
Humic acid †	†	237 233

* Values reported are for a reaction time of 1 hour. With reaction times of 4 hours, the values for the hydroxy acids were approximately 10 percent lower than theoretical.

† Dried at room temperature in vacuum over phosphorus pentoxide.

‡ Recrystallized from water and dried at 105° C.

§ Dried at 105° C.

For method of preparation see ref. 20.

|| Electrometric value, 235.

Complete methylation followed by hydrolysis has been used for the determination of hydroxyl and carboxyl groups in both natural and regenerated humic acids. Total methoxyl represents both carboxyl and hydroxyl groups. Methoxyl after hydrolysis is a measure of the hydroxyl groups and carboxyl can be obtained by difference, or directly, by determination of the alcohol liberated in the hydrolysis.²⁵ Dimethyl sulfate and alkali, methanol and hydrochloric acid,^{26, 43} and methanol and hydrochloric acid followed by diazomethane,²⁵ or diazomethane alone have been used in the methylation procedure. Because of the

insolubility of the humic acids in suitable solvents, complete methylation is difficult. Variations in methoxyl content under different conditions of methylation have been ascribed ²⁴ to shifting of tautomeric groups. Reports on the ratios of ester to ether methoxyl, ratio of carboxyl to hydroxyl groups have varied from 4:1 to 1:4. Bituminous coals contain negligible amounts of hydroxyl and carboxyl groups so that the presence of these groups in regenerated humic acids must be due to their formation during the oxidation procedure. Nothing is known as to the structures in the original coal from which they are derived.

Other than hydroxyl and carboxyl groups, no functional groups have been shown to be present in humic acids prepared by the oxidation of bituminous coal but the presence of carbonyl groups has been reported in the primary oxidation products of humic acids from brown coals.³⁵ When the oxygen found in the carboxyl and hydroxyl groups of a regenerated humic acid is compared with the total oxygen determined by ultimate analysis, a large discrepancy is observed, from a half to a third of the oxygen being unaccounted for. It appears probable that this oxygen is in cyclic or linear ether structures. Studies have been made with reagents which are believed to undergo specific reactions with these oxygen-containing rings, but the results so far have not been unequivocal.⁴⁴ Solubility in a benzyl alcohol solution of hydrogen chloride has been ascribed to oxonium salt formation by heterocyclic oxygen structures.²⁴ The establishment of the exact nature of this unaccounted-for oxygen would be of great interest.

Thermal Behavior. Humic acids prepared by oxidation of bituminous coal, like

⁴³ Galle, R. R., and Nikolaev, A. G., *J. Applied Chem., U.S.S.R.*, **12**, 923-33 (1939).

⁴⁴ Fuchs, W., and Horn, O., *Brennstoff-Chem.*, **12**, 251-2 (1931).

the natural acids, are relatively unstable thermally. A decrease in equivalent weight is observed on drying at temperatures up to 150° C indicating a loss of sorbed water or other nonacidic impurities. Regenerated acids, dried above 150° C, show increases of equivalent weight pointing to the loss of acidic groups by decarboxylation, and natural acids from brown coals appear to behave in a similar way.^{20, 29, 45}

On thermal decomposition, neither natural nor regenerated humic acids yield any considerable amount of volatile decomposition products other than gases. The solid residue remaining after decomposition, at temperatures as low as 300° C, is infusible, shows no alkali solubility, indicating complete loss of carboxyl groups, and is insoluble even in very active solvents like the dihydroxybenzenes.

Hydrogenolysis. Hydrogenolysis of regenerated humic acids at 350° C in the presence of a copper chromium oxide catalyst results in good yields of yellowish brown amorphous solids of low softening point. Solvent fractionation indicates a wide range of molecular species, from those soluble in petroleum ether to products insoluble in benzene. The higher-molecular-weight fractions show ²⁰ three- to fourfold differences in molecular weight between polar and nonpolar solvents. It thus seems probable that the strong associating properties of humic acids are not due alone to functional oxygen groups like hydroxyl and carboxyl, but may be ascribed in part, at least, to some characteristic nuclear structure.

The preceding paragraphs have indicated how meager is our information on these important intermediate oxidation products of bituminous coal, the regenerated humic acids. We can conclude, however, that

they are bodies of average molecular weight not greater than 1,000, of condensed cyclic structure, and that they contain sufficient hydrophilic groups, carboxyl and hydroxyl, to confer alkali solubility. Since they represent such a large part of the original coal structure more complete knowledge of their constitution is of the greatest importance from the standpoint of coal chemistry.

SOLUBLE ACIDS

As has been indicated in earlier paragraphs, the most important contributions to our knowledge of coal by oxidative degradation have come from studies of the soluble acids produced by further oxidation of the regenerated humic acids. This oxidation to the soluble acids may take place in one step, without isolation of the humic acids, or in two, involving an intermediate isolation of these acids. That the humic acids are an intermediate product there appears no doubt, although in very active oxidation procedures their existence may be only fleeting.

The ultimate oxidation products of the regenerated humic acids are carbonic acid, water, and so forth. Between the humic acids and these simple products there appears, however, a whole series of acids distinguished broadly from the regenerated humic acids by solubility in aqueous solution, neutral and acid as well as alkaline. Earlier workers gave these acids names,⁴⁶ largely on the basis of color or solubility. The reddish brown soluble acids formed in the early stages of oxidation of humic acids were called hymatomelanic acids, the golden yellow ones formed in the next step, fulvo acids. There have also been described ⁴⁷ two intermediate types of soluble acids between the humic acids and the ben-

⁴⁵ Stach, H., *Braunkohlenarch.*, No. 40, 1-51 (1933).

⁴⁶ See pp. 31-3 of ref. 33.

⁴⁷ See p. 444 of ref. 39.

zenecarboxylic acids. In view, however, of our very limited knowledge of the nature of these acids, it appears wiser for the time being merely to recognize that there lies between the regenerated humic acids and the crystalline, definitely characterizable types, such as oxalic and the benzenecarboxylic acids, a series of water-soluble acids of varying molecular complexity, characterized by colors ranging from reddish brown to golden yellow, having lower equivalent and molecular weights than humic acids, showing for the greater part solubility in organic solvents like ether, alcohol, and acetone, diffusing through parchment or cellophane, either with or without an applied electrical potential, having ultimate compositions indicating cyclic nuclei, and having, like the humic acids, oxygen unaccounted for in either carboxyl or hydroxyl groups, but usually with a very much smaller fraction of the total oxygen so unaccounted for. Neither the acids nor the methyl esters of these intermediate oxidation products have yet been obtained in crystalline form. Like the humic acids, they show marked thermal instability. Even their methyl esters are very incompletely volatilized in a molecular still. Repeated redistillation of the volatile fraction results in continued accumulation of resinous, and, if the temperature is increased sufficiently, carbonized, residues. This behavior distinguishes them very sharply from the methyl esters of the benzenecarboxylic acids.

The peculiar thermal behavior of these colored soluble acids, which are of intermediate complexity between the humic and the benzenecarboxylic acids, indicates the presence in their nuclear structures of other than simple carbon rings. These may be five- or six-membered carbon rings with active double bonds or heterocyclic compounds. Peripheral polar groups, like

hydroxyl or carboxyl, in special positions affect vapor pressure very greatly,⁴⁸ but methylation destroys such effects entirely so that the thermal instability of these compounds derived from coal cannot be accounted for by the presence of such groups. Investigations of the nature of the nuclear structure of these colored intermediate acids would be of great importance. They are of sufficient complexity so that any facts established would be of significance, and yet they appear simple enough so that available tools could effect a successful attack.

Oxidation in Acid Medium. Bituminous coals, or humic acids prepared from them, can be readily converted to these soluble acids by the action of such oxidizing agents as nitric acid, and aqueous solutions of permanganates, peroxides, and so forth, and molecular oxygen is an effective reagent on aqueous suspensions of coal at elevated temperatures and pressures. With the exception of nitric acid, the use of these oxidizing agents in other than *alkaline medium* results in poor yields of the simpler soluble types of organic acids and the conversion of a large fraction of the carbon to carbonic acid. To obtain the soluble organic acids in good yields it appears to be essential first to degrade the coal structure to units of the humic acid type and then to attack these individually in a homogeneous reaction. The behavior of oxidizing agents in an acid aqueous medium appears to parallel more closely the heterogeneous gas-solid reaction of oxidizing gases on coal at elevated temperatures, where, except under very special circumstances,⁴⁹ the formation of organic acids does not take place. It appears probable that this behavior is due to the very great

⁴⁸ See p. 1111 of ref. 38.

⁴⁹ Fischer, Franz, Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 184-7 (1933).

insolubility of regenerated humic acids in acidic aqueous media. Nitric acid constitutes a specific exception, probably because, at least in the higher concentrations, humic acids are soluble.

Oxidizing reactions carried out in acidic media have yielded only small amounts of definitely characterized products and unfortunately much of the work has been entirely qualitative.⁵⁰ A good part of the investigations have dealt with graphite and various types of carbon rather than with coals, but they are of interest in a general way.

It was found very early that, in addition to producing carbon dioxide and sulfur dioxide, concentrated sulfuric acid reacted on coals and charcoal with the formation of small amounts of organic acids.⁵¹ Pyromellitic acid, 1,2,4,5-benzenetetracarboxylic acid, was obtained in a 5 percent yield by distilling bituminous coal with concentrated sulfuric acid.⁵² Wood charcoal heated with concentrated sulfuric acid at 300° C has been reported to yield 1 to 2 percent of pyromellitic acid. A mixture of wood charcoal, concentrated sulfuric acid, and metallic mercury as a catalyst, when heated 5 to 6 hours at 290 to 315° C, was stated by Philippi and Thelen⁵³ to yield 6 to 7 percent of pyromellitic acid. These workers also found that "sulfuric acid carbons," which were obtained by heating aliphatic bodies like cellulose with sulfuric acid, behaved the same and concluded that for the final appearance of benzenepolycarboxylic acids preformed ring

systems were not necessary. They appeared to overlook the possibility that ring systems might be formed during the preliminary carbonization.

Although sulfuric acid reacts chiefly as an oxidizing agent, some sulfur is found in the oxidation product. However, sulfonic acid groups were shown not to be present, and for this reason early workers concluded⁵⁴ that there were no aromatic structures in coal. The absence of sulfonic acid groups has been confirmed by the failure of more recent workers⁵⁵ to obtain significant amounts of phenolic bodies by the action of fused alkali on "sulfonated" coals. It is of interest to note that the reaction products of sulfuric acid on coal possess strong base-exchange properties. As is to be expected, it has been found that higher-rank coals such as anthracite are markedly less reactive toward sulfuric acid than bituminous or brown coals. Interesting information dealing with the action of sulfuric acid as an oxidizing agent on coal has arisen recently from the observation that, unless very prolonged boiling periods were employed, nitrogen determinations by the Kjeldahl method were low. Beet⁵⁶ traced this difficulty to the formation of very resistant pyridinecarboxylic acids. After 72 hours of digestion, 20 percent of the nitrogen had not been converted to ammonium sulfate, and of this amount about a third was recovered as nitrogen-containing acids, which gave pyridine on heating and appeared to be largely nicotinic acid.

The reactions of carbon and of coals with mixtures of sulfuric acid with chromates, permanganates, and chlorates have been studied qualitatively by a number of

⁵⁰ A review of the more important results has been made by O. Horn, *Ges. Abhandl. Kenntnis Kohle*, **9**, 339-47 (1928-9).

⁵¹ Marchard, R. F., *J. prakt. Chem.*, **35**, 228-31 (1845).

⁵² Giraud, V., *Bull. soc. chim.*, (3), **11**, 389-91 (1894).

⁵³ Philippi, E., and Thelen, R., *Ann.*, **428**, 296-300 (1922). Philippi, E., and Rie, G., *ibid.*, **428**, 287-95 (1922).

⁵⁴ Pictet, A., and Bouvier, M., *Ber.*, **46**, 3342-53 (1913).

⁵⁵ *Dept. Sci. Ind. Research (Brit.)*, *Fuel Research Board Rept.*, **1938**, 51.

⁵⁶ Beet, A. E., *Fuel*, **19**, 108-9 (1940).

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⁴⁹ Fischer, Franz, Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 184-7 (1933).

insolubility of regenerated humic acids in acidic aqueous media. Nitric acid constitutes a specific exception, probably because, at least in the higher concentrations, humic acids are soluble.

Oxidizing reactions carried out in acidic media have yielded only small amounts of definitely characterized products and unfortunately much of the work has been entirely qualitative.⁵⁰ A good part of the investigations have dealt with graphite and various types of carbon rather than with coals, but they are of interest in a general way.

It was found very early that, in addition to producing carbon dioxide and sulfur dioxide, concentrated sulfuric acid reacted on coals and charcoal with the formation of small amounts of organic acids.⁵¹ Pyromellitic acid, 1,2,4,5-benzenetetracarboxylic acid, was obtained in a 5 percent yield by distilling bituminous coal with concentrated sulfuric acid.⁵² Wood charcoal heated with concentrated sulfuric acid at 300° C has been reported to yield 1 to 2 percent of pyromellitic acid. A mixture of wood charcoal, concentrated sulfuric acid, and metallic mercury as a catalyst, when heated 5 to 6 hours at 290 to 315° C, was stated by Philippi and Thelen⁵³ to yield 6 to 7 percent of pyromellitic acid. These workers also found that "sulfuric acid carbons," which were obtained by heating aliphatic bodies like cellulose with sulfuric acid, behaved the same and concluded that for the final appearance of benzenepolycarboxylic acids preformed ring

systems were not necessary. They appeared to overlook the possibility that ring systems might be formed during the preliminary carbonization.

Although sulfuric acid reacts chiefly as an oxidizing agent, some sulfur is found in the oxidation product. However, sulfonic acid groups were shown not to be present, and for this reason early workers concluded⁵⁴ that there were no aromatic structures in coal. The absence of sulfonic acid groups has been confirmed by the failure of more recent workers⁵⁵ to obtain significant amounts of phenolic bodies by the action of fused alkali on "sulfonated" coals. It is of interest to note that the reaction products of sulfuric acid on coal possess strong base-exchange properties. As is to be expected, it has been found that higher-rank coals such as anthracite are markedly less reactive toward sulfuric acid than bituminous or brown coals. Interesting information dealing with the action of sulfuric acid as an oxidizing agent on coal has arisen recently from the observation that, unless very prolonged boiling periods were employed, nitrogen determinations by the Kjeldahl method were low. Beet⁵⁶ traced this difficulty to the formation of very resistant pyridinecarboxylic acids. After 72 hours of digestion, 20 percent of the nitrogen had not been converted to ammonium sulfate, and of this amount about a third was recovered as nitrogen-containing acids, which gave pyridine on heating and appeared to be largely nicotinic acid.

The reactions of carbon and of coals with mixtures of sulfuric acid with chromates, permanganates, and chlorates have been studied qualitatively by a number of

⁵⁰ A review of the more important results has been made by O. Horn, *Ges. Abhandl. Kenntnis Kohle*, **9**, 339-47 (1928-9).

⁵¹ Marchard, R. F., *J. prakt. Chem.*, **35**, 228-31 (1845).

⁵² Giraud, V., *Bull. soc. chim.*, (3), **11**, 389-91 (1894).

⁵³ Philippi, E., and Thelen, R., *Ann.*, **428**, 296-300 (1922). Philippi, E., and Rie, G., *ibid.*, **428**, 287-95 (1922).

⁵⁴ Pictet, A., and Bouvier, M., *Ber.*, **46**, 3342-53 (1913).

⁵⁵ *Dept. Sci. Ind. Research (Brit.)*, *Fuel Research Board Rept.*, **1938**, 51.

⁵⁶ Beet, A. E., *Fuel*, **19**, 108-9 (1940).

workers.⁵⁷ The chief products of oxidation reported are carbon dioxide and monoxide. A recent paper pointed⁵⁸ out the formation of negligible amounts of complex oxygen-containing compounds with acid permanganate.

The action of sulfuric acid followed by hypobromite has been investigated⁵⁹ in some detail for a number of English coals. The first step in the oxidation was pictured as an attack on peripheral groups; the second, as reaction on condensed cyclic systems; and the residual nuclei were stated to show, by all the tests applied, the same composition and properties.

An early worker⁶⁰ found that Caro's acid, H_2SO_5 , reacted with all "Kohlen" very violently. Presumably carbon dioxide was the chief oxidation product.

The action of halogens on coal is partly addition, partly substitution,⁶¹ and, in the presence of aqueous alkali, strongly oxidizing.⁶² A mixture of hydrochloric acid and potassium chlorate, Hofmeister's reagent, has been used in studying the relative ease of oxidation of various coals.⁶³ Aqueous solutions of sodium chlorate, activated with osmium tetroxide, have been reported⁶⁴ to

react on a number of different types of carbon at 100° C with rapid formation of carbon dioxide, alkali-soluble products, and mellitic acid. No yields have been reported. Iodic acid was stated⁶⁵ to react on wood charcoal at 160, on bituminous coal and on coke at 180, on anthracite at 210, and on graphite at 240° C. Carbon dioxide was the only oxidation product reported. Diamond was not attacked at 260° C. A study has been made⁶⁶ of the action of chlorine dioxide on an Assam Tertiary coal from India. The analysis of this coal was: C 65.7, H 5.52, N 0.55, S 2.28, and O (by difference) 25.96 percent, respectively. The products of the oxidation were divided into water-soluble, ether-soluble, acetone-soluble, and residual material. Among the water-soluble products were found carbonic, oxalic, succinic, and maleic acids, benzoquinone and chloranil. The ether-soluble material was orange in color and was degraded further by fusion with potassium hydroxide at 180 to 200° C. In the soluble products from the fusion, oxalic, butyric, and maleic acids were identified and color reactions were obtained for protocatechuic acid. The insoluble products from the fusion were oxidized with alkaline permanganate, and the following acids were identified: acetic, butyric, oxalic, tartaric, hemimellitic, benzenepentacarboxylic, and mellitic. The acetone-soluble and the residual material were treated in the same way, and the same acids were isolated. Benzoquinone, chloranil, maleic acid, and tartaric acid had not hitherto been reported among the breakdown products of coal.

Chlorosulfonic acid, HSO_3Cl , has been

⁵⁷ Strache, H., and Lant, R., *Kohlenchemie*, Akademische Verlagsgesellschaft, Leipzig, 1924, p. 395. Simon, L. J., *Compt. rend.*, **178**, 495-S (1924). Florentin, D., *Bull. soc. chim.*, **35**, 228-30 (1924). Durand, J. F., *Compt. rend.*, **178**, 1822-4 (1924). Petrick, A. J., and Groenewoud, P., *J. Chem. Met. Mining Soc. S. Africa*, **38**, 370-83 (1938).

⁵⁸ Kreulen, D. J. W., *Brennstoff-Chem.*, **10**, 397-400 (1929).

⁵⁹ Pearson, A. R., *J. Soc. Chem. Ind.*, **42**, 68-72T (1923).

⁶⁰ Migault, W., *Chem.-Ztg.*, **34**, 337 (1910).

⁶¹ Stahlshmidt, A., *Z. angew. Chem.*, **12**, 790 (1899). Weiler, J. F., *Fuel*, **14**, 190-6 (1935). Cf. also Chapter S.

⁶² Hofmann, K. A., Schumpelt, K., and Ritter, K., *Ber.*, **46**, 2854-64 (1913).

⁶³ Francis, W., and Morris, H. M., *U. S. Bur. Mines, Bull.* **340** (1931), 44 pp.

⁶⁴ Hofmann, K. A., Ehrhart, O., and Schneider, O., *Ber.*, **46**, 1965 (1913).

⁶⁵ Ditte, A., *Ber.*, **3**, 325 (1870).

⁶⁶ Chowdhury, J. K., Bose, S. C., Karim, M. A., *J. Indian Chem. Soc., Ind. & News Ed.*, **3**, 1-12 (1940).

reported⁶⁷ to react with wood charcoal with the formation of carbon dioxide, carbon monoxide, sulfur dioxide, and hydrogen chloride. Sulfuryl chloride, SO_2Cl_2 , was stated to be without reaction on "Kohle" even at 100° C.

The action of ozone on bituminous coals deserves further investigation. Prolonged treatment of a finely ground, German (Westphalian) bituminous coal, suspended in water, at room temperature, has been shown⁶⁸ to convert 92 percent of the coal into water-soluble products. These were reported to be brown, acidic in reaction, and with a strong caramel odor. Other properties were not investigated. Less favorable results were obtained⁶⁹ by reaction in organic media, but glacial acetic acid was found more satisfactory than either chloroform or carbon tetrachloride.

Many investigations dealing with the action of nitric acid on coals and various forms of carbon have been carried out. The early work with nitric acid, or with mixtures of nitric acid and oxidizing salts, like potassium chlorate, was aimed at distinguishing between and classifying different carbonaceous materials such as lignite, coal, coke, amorphous carbon, wood, charcoal, and graphite. The products were merely examined qualitatively and described as yellow viscous liquids, humic acids, graphitic acids, and so forth, and in few experiments were definitely characterized products reported and in still fewer the amounts.⁷⁰

Oxalic acid and trinitroresorcinol⁷¹ have been reported in the oxidation products of

bituminous coal by concentrated nitric acid.

Mellitic acid has been obtained by the action of fuming nitric acid and potassium chlorate on graphite. Oxidation of wood charcoal by fuming nitric acid and potassium chlorate was found⁷² to give yields of approximately 25 percent by weight of the ammonium salt of mellitic acid, corresponding to 19.1 percent of the free acid, assuming the composition of the salt to have been $(\text{NH}_4)_2\text{C}_{12}\text{H}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$. A black amorphous intermediate oxidation product, resembling the "mellogen" of Bartoli and Papasogli,⁷³ was converted by alkaline permanganate into a mixture of oxalic and mellitic acids. It was stated that coal under these oxidation conditions gave only small yields of mellitic acid.⁷⁴

Donath and coworkers have studied the action of nitric acid on a variety of carbonaceous materials. A part of this work was carried out to develop methods of distinguishing between different ranks of coal and a part to establish the nature of the oxidation products. Nitric acid of specific gravity 1.055 was claimed to distinguish between brown and bituminous coals, the brown coal reacting strongly, the bituminous being unattacked.⁷⁵ From brown coal the following compounds were isolated: oxalic acid, propionic acid, butyric acid, and caproic acid. A "nitro" product was also mentioned. These workers suggested that a nitroso compound was formed when nitric acid reacted with coal.

The patent of Holliday and Silberrad⁷⁶ claimed that mellitic acid could be pre-

⁶⁷ Heumann, K., and Köchlin, P., *Ber.*, **15**, 416-20 (1882).

⁶⁸ Fischer, Franz, *Ges. Abhandl. Kenntniss Kohle*, **1**, 26-9 (1915-6).

⁶⁹ Fischer, Franz, and Tropsch, H., *ibid.*, **2**, 160-8 (1917).

⁷⁰ Berthelot, M. P. E., *Ber.*, **2**, 57-9 (1869).

⁷¹ Guignet, E., *Compt. rend.*, **88**, 590-2 (1879).

⁷² Dickson, G., and Easterfield, T. H., *J. Chem. Soc. (Proc.)*, p. 163, 1898.

⁷³ Bartoli, A., and Papasogli, G., *Gazz. chim. ital.*, **12**, 117-24 (1882).

⁷⁴ Compare ref. 106.

⁷⁵ Donath, E., and Bräunlich, F., *Chem.-Ztg.*, **28**, 180-2, 953-4 (1904).

⁷⁶ Holliday, R., and Silberrad, O., *Brit. Pat.* 24,662 (1908); *Ger. Pat.* 214,252 (1911).

pared in 90 percent yields by the action of nitric acid on charcoal. Later work^{58,77} has not substantiated this claim. Dimroth and Kerkovius⁷⁸ made an important contribution to our knowledge of the nature of the nitric acid oxidation products of carbonaceous materials by oxidizing charcoal with nitric acid, converting the acids to barium salts, and decarboxylating these salts by distillation with barium hydroxide. Benzene, naphthalene, and fluorene were found in the resulting hydrocarbons. This discovery of fluorene is the first and, to date, the only direct experimental evidence for the presence of condensed ring nuclei in the oxidation products of coals or carbons. Meyer and Steiner⁷⁹ made both pyromellitic and mellitic acids by oxidation of carbonaceous materials. The pyromellitic acid was prepared by distilling the raw reaction product obtained by heating charcoal and nitric acid with potassium acid sulfate. The yield was said to be 30 percent, but the basis on which the yield was calculated was not specified.

Mellitic acid in yields varying from 0 to 40 percent was said⁸⁰ to be prepared by refluxing carbonaceous materials with nitric acid, specific gravity 1.51, to which small amounts, 0.2 to 0.5 percent, of vanadic acid were added as a catalyst. The best yields were obtained from pine and fir charcoal. Charcoal which had been heated to white heat was stated to give no mellitic acid, graphite only traces, and brown coal, bituminous coal, and "Schungit," little or none. The amount of pure mellitic acid actually isolated was not stated, the yield of acid obtained being

⁷⁷ Juettner, B., *J. Am. Chem. Soc.*, **59**, 208-13 (1937).

⁷⁸ Dimroth, O., and Kerkovius, B., *Ann.*, **399**, 120-3 (1913).

⁷⁹ Meyer, H., and Steiner, K., *Monatsh.*, **35**, 391-405 (1914).

⁸⁰ Meyer, H., and Steiner, K., *Monatsh.*, **35**, 475-518 (1914).

estimated from the weight of crude ammonium salt recovered, which was purified by conversion to a copper salt.

Marcusson⁸¹ has studied the action of nitric acid of various concentrations on brown coal and found that approximately a third of the nitrogen added in the reaction could be split out again by refluxing with hydrochloric acid; for this reason he suggested that the nitric acid may have been held in oxonium structures.

The oxidation products of regenerated humic acids have been studied by Francis and Wheeler.⁴² These workers found that by the action of 30 percent nitric acid a yield of 25 percent of soluble acids, based on the humic acids, was obtained. Acetic, oxalic, succinic, picric, and pyromellitic acids were definitely identified among the oxidation products, and trimellitic acid was thought to be present. Approximately 3 percent of picric acid, based on the humic acids oxidized, was recovered.

Fuchs and Stengel⁸² have oxidized humic acids from Kassler brown coal, with 1 : 1 nitric acid. The yield of soluble acids was 643 grams from 900 grams of the humic acids, 71.5 percent, and after salt fractionation 645 grams of *organic* material was obtained; of this, 185 grams was recovered in the form of calcium salts insoluble in 1 : 1 hydrochloric or 1.85 *N* nitric acid, 25 grams as calcium oxalate, 395 grams as silver salt fractions, and 40 grams as nitrophenols, the fractions based on the original humic acids being 20.5, 2.78, 43.9, and 4.45 percent, respectively. The silver salt fractions were investigated by converting them to methyl esters by treatment with methanol and hydrogen chloride followed by diazomethane. The total yield of esters was

⁸¹ Marcusson, J., *Z. angew. Chem.*, **34**, 521-2 (1921).

⁸² Fuchs, W., and Stengel, W., *Ann.*, **478**, 267-83 (1930).

365 grams or 40.5 percent of the original humic acids. These were divided into ether-soluble and ether-insoluble fractions, the former being 20 percent, the latter 20.5 percent. The ether-insoluble esters could not be distilled in high vacuum. Two distillations of the ether-soluble material yielded 125 grams, 13.9 percent of the original humic acids. The following were identified with certainty: mellitic, benzenepentacarboxylic, pyromellitic (1,2,4,5-benzenetetracarboxylic), and trimesic (1,3,5-benzenetricarboxylic) acids. About 10 grams of the ester of the penta acid and 5 grams of each of the others were isolated. Thus, the oxidation product found in greatest amount, benzenepentacarboxylic acid, represented about 1 percent, and the total identified benzenecarboxylic acids, 2.7 percent, of the weight of the starting material. The amount of picric acid present, calculated from the weight of acridine picrate recovered, was 4.5 percent.

Prolonged treatment of bituminous coal with even 1 *N* nitric acid at its normal boiling point results in the formation of considerable amounts of soluble acids.⁵³ By oxidation of a Pittsburgh Seam coal with 1 *N* nitric acid for 32 days, 33 to 34 grams of soluble acids per 100 grams of coal was formed. Of this amount some 20 grams was found to be soluble in ether, acetone, or methanol. Methylation of the soluble acids with diazomethane, followed by distillation in a molecular fractionating still, up to bath temperatures of 300° C, yielded 10.8 grams of distillable esters per 100 grams of coal. No pure compounds were isolated from the products of this fractionation. In other experiments using salt fractionation followed by esterification and fractional distillation, small amounts

of mellitic and benzenepentacarboxylic acids were characterized as the methyl esters, 1 gram per 100 grams of coal of the former and 0.2 gram of the latter. In order to learn something of the nature of the nuclei of these acids, a 100-gram sample was decarboxylated by the method of Fischer and Schrader,⁵⁴ and the hydrocarbons formed were recovered and examined. About 9 grams of steam-volatile hydrocarbons was obtained. Of these, 40 percent boiled in the benzene range; higher hydrocarbons were also found, and the bomb smelled strongly of cresol and aromatic bases, and about 2.5 percent of a tarry residue, nonvolatile with steam but soluble in ether, was recovered from the bomb. All these facts point to the presence, even in these soluble acids, of nuclei other than the simple benzene ring. The gas, approximately 20 liters of which was recovered from the decarboxylation of 100 grams of these acids, consisted of 25 percent methane, 60 percent hydrogen, and small amounts of ethane and unsaturates. The presence of considerable amounts of the lower aliphatic hydrocarbons and hydrogen in the decarboxylation gases would indicate the presence of such aliphatic acids as oxalic, malonic, and succinic. These, however, although easy to isolate, were not found; hence, it seems probable that these gaseous products were derived from the breakdown of acids of complex nuclei.

Oxidation in Alkaline Medium. The most significant results obtained in the degradation of coal by oxidation reactions have been obtained in alkaline media. Rates of reaction in alkaline oxidizing media have also been shown^{55, 56} to be a useful criterion of rank.

⁵⁴ Fischer, Franz, and Schrader, H., *Ges. Abhandl. Kenntnis Kohle*, 5, 307-10 (1920).

⁵⁵ Olin, H. L., and Waterman, W. W., *Ind. Eng. Chem.*, 28, 1024-5 (1936).

⁵⁶ Niyogi, B. B., *Fuel*, 17, 228-9 (1938).

⁵³ Juettner, B., Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, 59, 236-41 (1937).

Early work indicated the formation of organic acids by the action of alkaline permanganate on various forms of carbon. Oxalic and mellitic acids were definitely identified.⁵⁷ Mellitic acid was shown to be one of the oxidation products of carbon anodes in alkaline electrolytes. Rods or plates made by carbonizing finely divided carbon, carbon black, retort carbon, or lampblack bound with tar were specified as suitable anodes. The reaction was limited to alkaline media.⁵⁸

Alkaline hypochlorites and hypobromites were used by early workers to oxidize various forms of carbon; carbon dioxide, oxalic acid, and mellitic acid have been reported among the oxidation products.⁵⁹ Experiments⁶⁰ with sodium hypobromite have resulted in the isolation of 2,4,6-tribromophenol and 2,4,6-tribromoaniline. The isolation of tribromoaniline is of special interest since it appears to be the first nitrogen compound, other than ammonia, to be isolated by oxidation.

Donath and coworkers in a study⁶¹ on the oxidation of known compounds found that most organic compounds which contain two "*Kohlenwasserstoffreste*" furnish, preponderantly, oxalic acid when oxidized with alkaline permanganate. Brown and bituminous coals were shown to furnish copious amounts of this acid when oxidized in the same way.⁶²

Franz Fischer and coworkers⁶³ have in-

⁵⁷ Schulze, Fr., *Ber.*, **4**, 502 (1871).

⁵⁸ Bartoli, A., and Papasogli, G., *Ber.*, **14**, 2241 (1881), **15**, 249 (1882), **16**, 1210 (1882). Löh, W., *Z. Elektrochem.*, **16**, 613 (1910).

⁵⁹ Bartoli, A., and Papasogli, G., *Gazz. chim. ital.*, **15**, 446-59 (1885).

⁶⁰ Dept. Sci. Ind. Research (Brit.), *Fuel Research Board Rept.*, **1935**, 32.

⁶¹ Donath, E., and Dietz, H., *J. prakt. Chem.*, **60**, 566-76 (1899).

⁶² Donath, E., and Margosches, B. M., *Chem. Ind.*, **25**, 226-31 (1902).

⁶³ Fischer, Franz, Schrader, H., and Treibs, W., *Ges. Abhandl. Kenntnis Kohle*, **5**, 267-91 (1920).

vestigated the nature of the oxidation products formed by the action of air at elevated temperatures and pressures on aqueous suspensions of various coals. Since temperatures of 200 to 250° C were employed in the oxidation, and since in this range the higher benzenecarboxylic acids

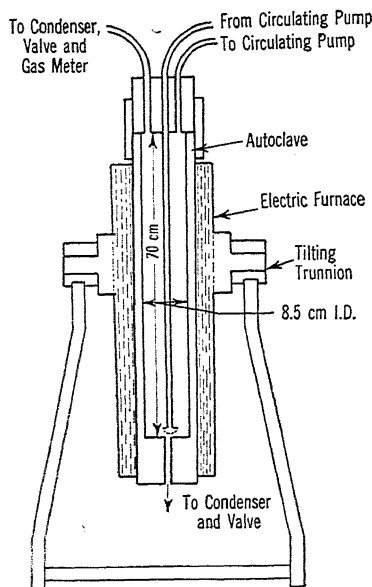


FIG. 4. Autoclave for pressure oxidation of coal with air.⁶⁴

are not stable, the particular acids isolated cannot be considered significant. The isolation and definite characterization of acids with the benzene ring as a nucleus are, however, of importance in indicating the nature of the carbon skeleton of coals. Apparatus typical of that used is illustrated in Fig. 4.⁶⁴ Later developments incorporated the compressor in the autoclave itself. Many experiments were carried out to study the effects of such variables as temperature, oxygen partial pressure, rate of air flow, and time. Data typical of the

⁶⁴ Fischer, Franz, *ibid.*, **4**, 13-25 (1919).

results with a bituminous coal are given in Table IV.

In oxidation I, a "mild" oxidation, 1,000 grams of the finely divided *Magerkohle*, Flöz Mausegatt, was suspended in 2.5 liters of 2.5 *N* sodium carbonate, 6.25 equivalents,

duced the acids precipitable on acidification. The total organic acids were also reduced from 4.86 equivalents to 1.5. The total amount of organic acids, based on the original coal, actually identified, was very small, 3.56 grams per 100 grams of coal

TABLE IV
OXIDATION OF AQUEOUS ALKALINE SUSPENSIONS OF
COAL WITH OXYGEN AT ELEVATED PRESSURES ⁹⁵

	I	II
Insoluble residue	202 grams	...
Total organic acids	4.86 equivalents	1.5 equivalents
Total steam-volatile acids
Benzoic acid	2.8 grams	4.3 grams
Acids precipitated by acidification	65.3 grams	5.0 grams
Acids easily extracted from filtrate with ether	148 grams	20.0 grams
Isophthalic acid	2.68 grams	Phthalic anhydride 3.0 grams
Phthalic acid	6.12 grams	Acids from difficultly soluble barium salts 5.5 grams
Acids difficultly extracted with ether—Total	21.32 grams	
Acids forming water-soluble calcium salts	2.8 grams	
Acids forming insoluble calcium salts (chiefly oxalic acid)	4.26 grams	
Benzenepentacarboxylic acid	4.66 grams	
Acids forming calcium salts soluble in acetic acid	6.0 grams	
Acids forming barium salts soluble in water	1.7 grams	
Mellitic acid	Copious amounts	

and was oxidized with air supplied at 60 atmospheres, passed at the rate of 400 liters per hour until 77.75 percent of the alkali carbonate had been converted to salts of organic acids. In oxidation II, a "strong" oxidation, conditions were the same, but the time of oxidation was increased to 68.5 hours. At the end of 26.5 hours all the carbonate had reacted and an additional 1.25 equivalent was added.

It will be observed from the data in the table that the longer oxidation period eliminated the unattacked residue and re-

dissolved, exclusive of mellitic acid, in experiment I and 1.30 grams per 100 grams of dry coal in II.

It was found ⁹⁵ that much better yields of benzenecarboxylic acids could be obtained if the products from the pressure oxidation were subjected to a "pressure heating" operation at 400° C since "thereby the polybasic acids were converted for the greater part to isophthalic and benzoic acids and the latter can be recovered easily

⁹⁵ Fischer, Franz, and Schrader, H., *Ges. Abhandl. Kenntnis Kohle*, 5, 200-10 (1920).

from solution." By this means the amount of acids actually characterized was greatly increased. The total amount of aromatic acids—only benzoic and isophthalic acids were found after this treatment—reached a maximum of 11.92 grams per 100 grams of dry, ash-free coal dissolved in a 200° C oxidation followed by a 400° C pressure heating treatment. Although these acids represent only a small fraction of the carbon in the coal, the work definitely established the presence of aromatic structures in bituminous coal. There is some question, however, whether the pressure heating treatment is only a decarboxylation of the higher to the lower benzenecarboxylic acids. A yield of 8.67 grams of benzoic and 3.25 grams of isophthalic acids, if decarboxylation of the higher acids is the only reaction

involved, means that there must have been present some 26.9 grams of benzenepentacarboxylic acid or 31.0 grams of mellitic acid. Mellitic acid is especially easy to isolate through its ammonium salt, and the penta acid is not difficult. It therefore seems highly improbable that the relatively large yields of isophthalic and benzoic acids reported depend entirely upon a simple decarboxylation of higher acids.

The results of pressure oxidation and pressure heating experiments⁹⁶ on cellulose, lignin, and brown and bituminous coals are summarized in Table V. As was to be expected, cellulose furnished aliphatic acids, and lignin, brown coal, and bituminous coals, mixtures of aliphatic and aro-

⁹⁶ Fischer, Franz, *Ges. Abhandl. Kenntnis Kohle*, 8, 371-83 (1924-7).

TABLE V
PRESSURE OXIDATION OF VARIOUS MATERIALS⁹⁶

	Volatile Acids *	Nonvolatile Acids *	Acids Identified *	
	percent	percent	percent	
Cellulose	28	14	0.7	Fumaric
				Maleic
			5.0	Oxalic
Lignin	11	34	0.3	Mellitic
			3.7	Benzenepentacarboxylic
			7.2	Oxalic
Brown coal	14	34		Mellitic
				Benzenepentacarboxylic
				Pyromellitic
				o-Phthalic
				Benzoic
Bituminous coal	Not terminated	30	0.58	Benzenepentacarboxylic
			0.93	Trimesic
				Phthalic
			0.33	Isophthalic
			0.35	Benzoic
			11.00	Benzoic and phthalic

* The figures for volatile and nonvolatile acids were stated to be approximate. The 11.00 percent of benzoic plus phthalic acids was obtained by pressure oxidation followed by pressure heating.

matic acids. Fischer and Schrader⁹⁷ regarded the fact that the bituminous coals yielded significant amounts of aromatic acids on oxidation as evidence for the point of view that such coals are derived from lignin, since in parallel oxidation experiments aromatic acids were recovered from it but not from cellulose. It has recently been shown,⁹⁸ however, that, during the thermal decomposition of cellulose, C₆ ring structures are formed rapidly at moderate temperatures. Hence, the establishment of the presence of aromatic structures in bituminous coal does not necessarily exclude cellulose as a progenitor of such coals.

Bone and coworkers have published a number of important papers^{22, 99, 100, 101} dealing with the action of alkaline permanganate on a series of coals and related substances. In the early work, the oxidation was carried out under pressure at higher than normal boiling temperatures; in the later work, in open vessels. The finely ground material was suspended in aqueous potassium hydroxide, the ratio of alkali to substance to be oxidized being 1.6, and solid potassium permanganate was added in small portions at a time to the boiling suspension. The amount of permanganate added determined the extent of the oxidation. With benzene extraction residues¹⁰² from bituminous coals a permanganate ratio

of approximately 8 was found to convert the residue to water-soluble acids. Somewhat higher ratios, up to 12, were actually employed.

Quantitative determinations were made of the distribution of the carbon among the oxidation products, and a number of the acids were isolated and definitely characterized. Typical data on carbon distributions are given in Table VI. Although not so stated, the fraction of the carbon classified as "benzenecarboxylic" was a difference quantity and represented that fraction of the carbon not found in such simple readily determinable forms as acetic, oxalic, or carbonic acids. These acids are probably "benzenoid," but only a fraction are of the benzenecarboxylic series.

In an earlier paper,¹⁰³ it was concluded erroneously that the fraction of the carbon appearing as benzenoid acids was the same regardless of the rank of the coal. This was corrected in a later paper,¹⁰⁴ and the relation between benzenoid carbon and rank, evident from the above data, is one of the most important relations which has been brought out by oxidation studies.

The isolation of all the benzenecarboxylic acids except benzoic was reported. Unfortunately, no statement was made as to the purity or the amounts isolated in any except the first paper, where the isolation of 1.6 grams of mellitic acid per 100 grams of coal substance was reported. In view of later work it seems probable that the recovery of any individual acid never amounted to more than a few grams per 100 grams of coal substance and often it was probably less than 1 gram per 100 grams. The inference which the reader is likely to make from the carbon balance data, that up to 46 percent of the carbon of a bituminous coal, for example, can be

⁹⁷ See pp. 208, 551 of ref. 95 and p. 373 of ref. 96.

⁹⁸ Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **59**, 234-6 (1937). See also Berl, E., and Koerber, W., *Ind. Eng. Chem.*, **32**, 676-7 (1940).

⁹⁹ Bone, W. A., and Quarendon, R., *Proc. Roy. Soc. (London)*, **110A**, 537-42 (1926).

¹⁰⁰ Bone, W. A., Parsons, L. G. B., Sapiro, R. H., and Groocock, C. M., *ibid.*, **148A**, 492-522 (1935).

¹⁰¹ Bone, W. A., and Bard, B. J. A., *ibid.*, **162A**, 495-501 (1937).

¹⁰² It was stated that the residues from benzene extractions were used to facilitate the oxidation, but that similar results were obtained with the whole coal.

¹⁰³ See p. 493 of ref. 22.

¹⁰⁴ See p. 514 of ref. 100.

TABLE VI

CARBON DISTRIBUTION AMONG ACIDS FORMED BY ALKALINE
PERMANGANATE OXIDATION OF VARIOUS SUBSTANCES¹⁰⁰

	Lignin	Peats	Brown Coals and Lignites	Bituminous Coals	Anthracites
Percent of carbon as:					
Carbonic acid	57-60	49-61	45-57	36-42	43
Acetic acid	2.7-6.0	3.1-5.6	3.0-7.5	1.7-4.6	2
Oxalic acid	21-22	15-28	9-23	13-14	7
Benzenecarboxylic acids *	11.8-15.8	10-25	22-34	39-46	50

* These workers used the terms "benzenecarboxylic acids" and "benzenoid acids" interchangeably. These acids are probably "benzenoid," but only a part are the simple acids consisting merely of a benzene nucleus and carboxyl groups.

recovered as a mixture of benzenecarboxylic acids, is erroneous. Such a recovery would amount to approximately 90 grams of benzenecarboxylic acids per 100 grams of coal substance, assuming the average content of 50 percent carbon reported for the mixed acids, and it seems incredible that, if we were dealing simply with a mixture of the benzenecarboxylic acids, the recoveries should be only a few grams per 100 grams of coal. Furthermore, general criteria for the benzenecarboxylic acid series can be applied to these mixed acids. All benzenecarboxylic acids yield benzene on decarboxylation, and the methyl esters of all are stable and can be easily distilled. The yields of benzene on decarboxylation of the mixed acids are about a third those which would be obtained if we were dealing with a mixture of benzenecarboxylic acids, and, along with the benzene, are obtained benzene homologs and phenolic compounds indicating the presence of more complicated cyclic structures. The papers of Bone and coworkers, as well as later investigators,¹⁰⁵ have indicated that a large fraction of the methyl esters of these mixed acids is not distillable even under conditions where the

methyl ester of the benzenecarboxylic acid of highest molecular weight, hexamethyl mellitate, distills rapidly and without decomposition.

Oxidation of a Pittsburgh Seam bituminous coal and its 500° C coke, with alkaline permanganate,¹⁰⁵ gave the distribution of the carbon among the various oxidation products shown in Table VII. More than 90 percent of the carbon of the coal was recovered as water-soluble acids; the balance was lost either as volatile compounds during the oxidation process or remained unattacked. The free acids were recovered either by electrolytic decomposition of the

TABLE VII

CARBON DISTRIBUTION AMONG OXIDATION
PRODUCTS OF A PITTSBURGH SEAM COAL AND
ITS 500° C COKE¹⁰⁵

	Pittsburgh Seam Coal	500° C Coke
Percent of carbon as:		
Carbonate	45.0	40.7
Acetate	2.2	1.6
Oxalate	15.0	11.6
Salts of aromatic acids	30.8	37.1
Total carbon recovered as alkali salts, per- cent	93.0	91.0

¹⁰⁵ Juettner, B., Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **59**, 236-41 (1937).

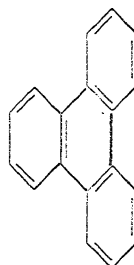
salts in a three-compartment cell or by continuous liquid-phase extraction. The recovery of "aromatic" carbon by electrolysis was approximately 95 percent of that indicated to be present by analysis of the salts.

Conversion of the acids from a Pittsburgh Seam coal to their methyl esters and fractionation of these esters in vacuum resulted in the isolation of only one crystalline compound, dimethyl oxalate. Salt fractionation, followed by esterification and vacuum fractional distillation, resulted in the isolation of small amounts, less than a gram per 100 grams of coal, of the methyl esters of mellitic, pentacarboxylic, and terephthalic acids. Somewhat greater amounts were obtained from the acids from the 500° C coke. In conclusion it was stated that "a significant fraction, 50 to 60 percent, of the nonvolatile acids formed by alkaline permanganate oxidation of this coal and its 500° C coke, is aromatic. We have, however, found no evidence that any considerable amount of simple benzenoid acids is present."

A study¹⁰⁶ has been made of the effect of various oxidation procedures on the yields of mellitic acid from coals, cokes, and graphite. The amounts of mellitic acid formed, based on the weight of ammonium salt recovered, by various oxidation procedures on a 500° C coke were as follows: prolonged boiling, 286 hours, with alkaline permanganate, 3.37 grams; 336 hours refluxing with nitric acid (specific gravity, 1.5), 7.25 grams; nitric acid followed by alkaline permanganate, 11.9 grams; nitric acid followed by acid permanganate and then by alkaline permanganate, 10.9 grams. There was evidently little to choose between the last two procedures from the standpoint of yield, but the nitric acid plus

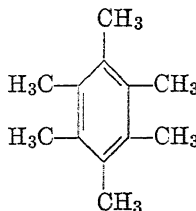
alkaline permanganate procedure was adopted because of simplicity. The reproducibility was shown to be satisfactory, the total acids recovered by electrolysis in three oxidations on a 500° C coke, from a Pittsburgh Seam coal, being 29.7, 30.8, and 28.8 grams per 100 grams of coke, and the mellitic acid 11.9, 11.5, and 11.5 grams. The results of the application of this method to a series of carbonaceous materials are shown in Table VIII.

In the series from Illinois coal to natural graphite there is a general increase in the yield of mellitic acid with rank. Mellitic acid can be formed only by oxidation of condensed carbocyclic structures, of which the simplest which has been shown to furnish mellitic acid on oxidation is



triphenylene

or of compounds having a benzene ring completely alkylated such as



hexamethylbenzene

or of mixtures of these two types of compounds. Since both ultimate composition and behavior on pyrolysis indicate a decrease rather than an increase in aliphatic structures in higher-rank materials (none at all is, of course, present in graphite), the

¹⁰⁶ Juettner, B., *J. Am. Chem. Soc.*, **59**, 208-13, 1472-4 (1937).

TABLE VIII

DATA ON OXIDATIONS BY NITRIC ACID FOLLOWED BY ALKALINE PERMANGANATE ¹⁰⁰

Materials *	Carbon per 100 Grams grams	Residue after Nitric Acid Oxidation grams	Total Acids after Permanganate Oxidation grams	Mellitic Acid Recovered grams
<i>Coals and Graphite</i>				
Illinois No. 6 Seam coal	69.50	68.0	19.3	4.3
Pittsburgh Seam coal	78.27	70.1	28.1	5.5
High Splint Seam coal	78.70	53.2	14.4	5.0
Pocahontas No. 3 Seam coal	85.10	92.4	25.8	10.9
Anthracite coal	82.87	77.2	32.6	17.7
Natural graphite	97.40	78.5	26.9	21.7 †
<i>1,000° C Cokes</i>				
Illinois No. 6 Seam	83.78	52.3	26.2	19.4
Pittsburgh Seam	86.74	50.9	29.4	22.5
High Splint Seam	89.96	48.1	28.3	20.8
Pocahontas No. 3 Seam	88.68	49.5	30.5	22.1
Anthracite	87.73	48.6	26.1	19.8
<i>Other Cokes and Chars</i>				
Pittsburgh Seam, 500° C	80.17	95.5	29.7	11.9
Pittsburgh Seam, 700° C	79.80	79.4	39.7	24.1
Domestic coke	84.23	46.6	27.5	19.8
Metallurgical coke	80.28	48.3	27.2	17.9
Cellulose char, 1,000°	91.59	39.5	30.0	24.8
Active carbon	83.10	39.0	33.1	19.7
Carbon black	93.91	56.5	42.9	32.2
Petroleum coke	92.31	139.6	49.9	20.7
Coke from low-temperature pitch, 700° C ‡	88.05	99.2	47.3	22.9
<i>Pitches and Known Compounds</i>				
Pitch from low-temperature tar §	83.52	84.5	22.0	4.1
Pitch from high-temperature tar ¶	91.52	135.5	23.0	7.9
Triphenylene	94.70	169.6	77.8	67.2
Hexaethylbenzene	87.72	11.0	2.9	0.0

* 100 grams used in each case.

† 7.6 grams of unoxidized graphite remained.

‡ Prepared by carbonizing the pitch from the low-temperature tar at 700° C.

§ The residue remaining at 400° C from the distillation of tar from a low-temperature carbonization process.

¶ The residue remaining at 400° C from the distillation of tar from a high-temperature carbonization process.

most reasonable interpretation of the increased yield of mellitic acid with rank is that it reflects an increase in the amount of condensed carbocyclic structures in the higher-rank materials. It is obvious, however, that there will be a certain structure from which the maximum yield of mellitic acid would be expected. From triphenylene, 12 out of the 18 carbon atoms present in the hydrocarbon could appear in mellitic acid. From coronene, the maximum would be 12 out of 24, and with larger condensed structures the fraction of the carbon appearing as mellitic acid would become smaller and smaller until such a size was reached that conceivably the oxidation would effect a scission and more than one molecule of mellitic acid could be formed per molecule of hydrocarbon.

The general similarity of the yields of mellitic acid from the 1,000° C cokes indicates that at this temperature all specific characteristic structural differences of the original substance are eliminated.

The results of oxidation of a Pittsburgh Seam coal and of cokes prepared from it at 500, 700, and 1,000° C show a greatly increased yield of mellitic acid from coke carbonized at 700° C as compared with the raw coal, but little change between 700 and 1,000° C. The rapid change up to 700° may be due not only to formation of condensed carbocyclic from aliphatic and heterocyclic structures but also to the conversion of hydroaromatic to aromatic rings by loss of hydrogen.

The yield of mellitic acid obtained from a high-rank coal such as anthracite indicates a degree of condensation of the same order as a coke prepared by heating a bituminous coal to at least 700° C. The relatively small increase in yield of mellitic acid obtained by oxidation of anthracite which had been heated to 1,000° C as compared with the unheated coal also indi-

cates that a very complete degree of condensation to carbocyclic structures has been reached in the anthracite.

The high yields of mellitic acid from domestic and metallurgical cokes, carbon black, petroleum coke, and coke from low-temperature pitch all reflect a structure consistent with the temperatures of their preparation. The exceptional yield from carbon black is probably related to its very small crystal size. It appears likely that the attack in the individual planes in a graphitic structure is largely peripheral, with the formation of carbon dioxide exclusively, so that only one molecule of mellitic acid would be obtained from that part of any given plane in which all the carbon atoms are connected by primary valence forces. Obviously, the smaller such a unit, the greater the fraction of the carbon appearing as mellitic acid and the less as carbon dioxide.

The pitches gave rather poor yields of mellitic acid, owing, no doubt, to their rather small content of molecules of either condensed carbocyclic or substituted carbocyclic structures of proper configuration. The lower yield from the low-temperature pitch may be ascribed to its higher hydroaromatic content.

The yield of mellitic acid from triphenylene, the simplest purely cyclic structure from which it has been prepared, was 44.8 percent of theory. Hexaethylbenzene, by this oxidation procedure, formed carbon dioxide almost exclusively, and no mellitic acid was recovered.

This work on the relation between the yield of mellitic acid and the rank of carbonaceous materials represents one of the most important contributions to our knowledge of coal which has been made by oxidation studies. An equally important step would be the determination of the amounts and the nature of the other aromatic acids

formed. These, in the lower-rank carbonaceous materials, constitute a greater fraction of the oxidation products than mellitic acid.

Interesting work with this end in view, dealing with the action of alkaline permanganate on some Australian coals, has been published.¹⁰⁷ The coal used was Australian "Proprietary," with the following properties: moisture 22.7, ash on dry basis 7.25, and volatile matter at 900° C on dry, ash-free basis, 31.65 percent. The ultimate composition on the dry, ash-free basis was: C 78.65, H 3.95, N 1.40, S 0.30, and O (difference) 15.7 percent. The coal was stated to be unusually rich in fusain.

The general procedure in the oxidation was the same as that of Bone and co-workers. An alkali-coal ratio of 1.6 was used and a permanganate-coal ratio of 10.4, both on the basis of dry, ash-free coal. Conversion of the figures to the ash-free-coal basis shows that the total yield of dry,

crude acids recovered from the oxidation was 67.0 grams per 100 grams of coal. Esterification yielded 56.7 grams of methyl esters. From these, after dilution with ethanol and standing for several weeks, there separated 5.12 grams of crystalline esters. The balance of the esters was fractionated in high vacuum and yielded 23.5 grams in ten fractions up to 241° C, at which temperature there was incipient decomposition. The results of the separation are given in Table IX. All the figures have been converted to grams of acids per 100 grams of dry, ash-free coal. The total amount of benzenecarboxylic acids separated and definitely identified from this coal was 26.38 grams per 100 grams of dry, ash-free coal. The large amounts of tri, tetra, and penta acids, 80 percent of the total identified, indicated that, in this coal, structures consisting of benzene rings with three, four, or five carbon atoms attached predominated. The large amount of fusain may be responsible for the con-

¹⁰⁷ Kent, C. R., *Fuel*, **19**, 119-25 (1940).

TABLE IX

OXIDATION PRODUCTS OF AN AUSTRALIAN COAL¹⁰⁷
(grams per 100 grams of dry, ash-free coal)

	Dic Acids		Benzenecarboxylic Acids *										Penta-	Hexa-
	Oxalic	Succinic	Di-			Tri-		Tetra-						
			<i>o</i>	<i>m</i>	<i>p</i>	1,2,3	1,2,4	1,2,3,4	1,2,3,5	1,2,4,5	Mixed			
Separated as crystalline esters before distillation	0.03	2.46	0.39	
From fractional distillation of esters	0.29	0.09	0.51	0.42	0.10	1.30	3.30	0.56	1.70	0.20	3.23	
Crystallized from non-distillable residue	8.38	3.12	
Totals	0.29	0.09	1.33			4.60		5.72				10.84	3.51	

* These acids are named as follows: dicarboxylic—phthalic (*o*), isophthalic (*m*), terephthalic (*p*); tricarboxylic—hemimellitic (1,2,3), trimellitic (1,2,4); tetracarboxylic—prehnitic (1,2,3,4), mellophanic (1,2,3,5), pyromellitic (1,2,4,5); pentacarboxylic; hexacarboxylic—mellitic.

siderable fraction of penta and mellitic acids recovered. Fusain has a sufficiently high carbon-hydrogen ratio to indicate a highly condensed cyclic structure. In triphenylene the atomic ratio is 1.5; in the fusain from this Australian coal it is 1.84.

A comparison of the distribution of the carbon among the oxidation products of this coal—41.5 percent as CO_2 ; 0.3 percent as acetic acid; 7.3 percent as oxalic acid; and 50 percent as aromatic acids—with Bone's data for the lignin, peat, anthracite series shows that the data for this Australian coal do not readily fit into the series. The high benzenoid carbon and low oxalate correspond most nearly with anthracite. As the author suggests, the observed anomaly may well be due to the presence of considerable fusain in the Australian coal.

The action of oxygen, at elevated temperatures, on aqueous alkaline suspensions of a number of coals and related carbonaceous materials has been studied.¹⁰⁸ Temperatures from 100 to 250° C and oxygen partial pressures of 100 to 375 pounds per square inch, 7 to 25 atmospheres, were investigated. Below 225° C, the reaction rate was found to be very slow. The apparatus used is shown in Fig. 5. Sufficient alkali was employed to absorb all the carbon dioxide formed, and a constant partial pressure of oxygen was furnished from a pressure cylinder. The rate of formation of the various oxidation products was similar to that observed with nitric acid. An increase in area of gas-liquid interface, by the introduction of packing material into the bomb, was found to increase significantly the reaction rate in early stages of the degradation. The substitution of sodium hydroxide for potassium hydroxide

had an adverse effect on reaction rate, probably owing to differences in solubility of the sodium and potassium salts of the primary oxidation products. The rate was very slow with calcium hydroxide alone,

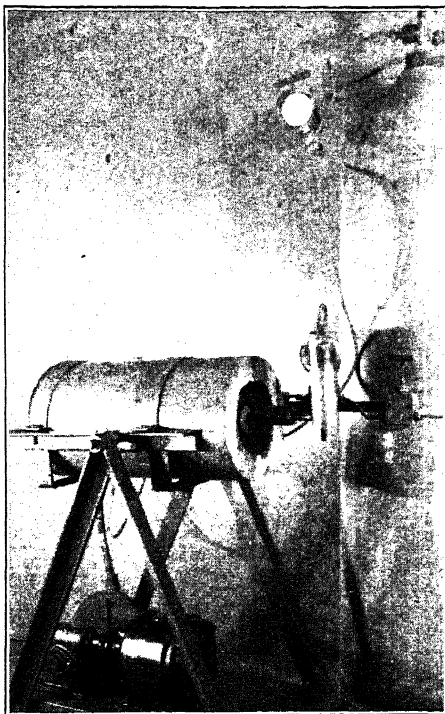


FIG. 5. Apparatus for oxidation of bituminous coal to organic acids by oxygen at elevated temperatures and pressures.¹⁰⁸

but a large part of the potassium hydroxide could be replaced by calcium hydroxide without adverse effect. Tests on some twenty different oxidation catalysts indicated positive effects only with copper and cobalt salts. These catalysts appeared to have little effect on the rate of initial oxidation but accelerated markedly the conversion of the soluble acids to carbon dioxide and water. The distribution of the carbon among the oxidation products for

¹⁰⁸ Smith, R. C., Tomarelli, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **61**, 2398-402 (1939).

a number of oxidations at 225° C and 600 pounds total pressure is summarized in Table X.

Bituminous and anthracite coals and low-temperature coke could be oxidized completely to carbon dioxide and water or to any desired intermediate stage. The 700° C coke, high-temperature coke, graphite, and pitch were incompletely oxidized, 50 to 60

and the graphite incompletely attacked. This indicates the very different courses which an oxidation may take with different carbonaceous materials and emphasizes the necessity for caution in using a reactivity test which depends only on measurement of the rate of carbon dioxide formation.

The usual methods of salt fractionation, esterification, and fractional distillation of

TABLE X^{1,2}
OXIDATIONS OF AQUEOUS ALKALINE SUSPENSIONS OF
CARBONACEOUS MATERIALS WITH OXYGEN AT ELEVATED PRESSURES *

	Total Soluble Carbon percent	Carbon- ate Carbon percent	Oxalate Carbon percent	"Aro- matic" Carbon percent	Ratio of Carbon- ate Carbon to Soluble Carbon Carbon	Carbon- ate Carbon grams	"Aro- matic" Carbon grams
Illinois No. 6 Seam coal	100.2	58.1	9.33	32.8	0.58	20.3	11.4
Pittsburgh Seam coal	98.8	49.7	12.90	36.2	0.50	19.2	14.0
High Splint Seam coal	102.2	57.7	8.03	36.5	0.56	22.7	14.3
Pocahontas No. 3 Seam coal	100.6	57.0	4.50	39.1	0.52	24.2	16.6
Anthracite coal	100.5	59.3	3.40	37.8	0.59	24.5	15.6
500° C coke	99.5	61.3	5.20	33.0	0.62	24.5	13.2
700° C coke	85.5	59.8	4.15	21.5	0.71	24.6	8.2
High-temperature coke	72.7	63.1	2.90	6.7	0.87	25.6	2.7
Graphite 40 grams	62.1	57.9	1.90	2.3	0.92	28.8	1.1
Pitch 30 grams	80.5	44.0	6.45	30.0	0.55	12.0	8.2

* The sources of these materials are given in Table VIII.

percent of the carbon appearing as carbon dioxide and much smaller amounts of organic acids being recovered. With graphite, no significant amount of organic acid was obtained because mellitic acid, the principal organic acid formed from the oxidation of graphite, was found to be unstable under the conditions of this oxidation. It is interesting to note that under the same conditions approximately a third more carbon dioxide was evolved from the unreactive graphite than from the low-rank reactive Illinois coal, although the coal was completely converted to soluble products

the esters were applied in separating the acids. Oxalic, trimellitic, pyromellitic, prehnitic, and terephthalic acids were identified. The trimellitic acid appeared to predominate. The absence of pentacarboxylic and mellitic acids was ascribed to their partial decarboxylation at the temperature employed. As in the work with alkaline permanganate, it was found that a significant fraction of the esters could not be distilled under conditions where the least volatile of the esters of the benzene-carboxylic acids, the hexamethyl mellitate, distills rapidly, thus indicating the presence

of acids other than those with a simple benzene nucleus.

Oxidation of Petrographic Constituents. The whole problem of the nature of the oxidation products of the petrographic constituents should be investigated completely. One study,¹⁰¹ using alkaline permanganate on a series of "bright," "dull," and "fusain" samples from British coals, has indicated little difference in the distribution of the carbon among the oxidation products. In general, the samples of "dull" coal showed a somewhat higher fraction of carbon as benzenoid acids and a lower yield of oxalate. Results for two fusains gave lower results for benzenoid carbon than was noted for the samples of bright coal. It was stated that, "while their resistance to oxidation markedly increased in the order 'bright' → 'dull' → 'fusain,' no great difference was observable either qualitatively, as between the resultant products, or quantitatively, as regards the distributions of the original carbon between them, save only that the percentage yielded as carbon dioxide, by 'fusain,' was always materially greater than that yielded by either of the other two constituents."

Samples of Illinois fusain, oxidized by nitric acid and alkaline permanganate, have yielded¹⁰ an average of 27 grams mellitic acid per 100 grams of fusain, and fractional distillation data on the methyl esters of the other acids have indicated a predominating amount of the penta acid. The oxidation products of this fusain sample correspond to a structure with a high degree of condensation to six-membered rings. This is in accord with the view that fusain has been formed at a considerably higher temperature than the bulk of the coal.

Complex Soluble Acids. The nature of the highly colored soluble acids formed in the mild oxidation of "regenerated humic

acids" has recently been investigated.¹⁵ Humic acids of definite composition prepared by the action of air at elevated temperatures were further oxidized in alkaline permanganate, using a permanganate : humic acid ratio of 2.5. About 50 percent of the humic acids was converted to reddish brown water-soluble acids. Small amounts of oxalic and mellitic acids were isolated, but the yields were not stated. The mixture of acids was converted to methyl esters, but it was found that only a small proportion of these could be distilled even at 250° C under a pressure of 0.01 millimeter. Fractionation of the esters with solvents showed less than 8 percent soluble in petroleum ether; from this fraction, dimethyl oxalate and hexamethyl mellitate were isolated; 82 percent was insoluble in petroleum ether but soluble in benzene, and the balance was insoluble in benzene. The composition of the benzene-soluble esters was carbon 58.86 and hydrogen 4.9 percent; and the atomic ratio of carbon to hydrogen was unity. This carbon-hydrogen ratio is exactly that for the methyl esters of the benzenecarboxylic acid series, and the carbon and hydrogen content corresponds to a mixture of approximately one-third of the dimethyl and two-thirds of the trimethyl esters of the corresponding benzenecarboxylic acids. The methyl esters of both the di and tri acids can, however, be rapidly distilled in a molecular still at temperatures as low as 100° C. This work confirms the results of other investigators in indicating that even the water-soluble types of acids produced by oxidation of bituminous coal must have a nucleus of other than simple benzenoid character. It also emphasizes the danger of assuming that a mixture of acids of approximately the same ultimate composition as those of the benzenecarboxylic acid

series consists, necessarily, entirely of acids of that series.

CONCLUSION

Mild oxidation of bituminous coals results in degradation to a mixture of relatively simple units, the "humic acids." Although these primary oxidation products have not yet been definitely characterized, they are certainly of condensed cyclic structure, some of the cycles containing only carbon atoms, others probably oxygen, nitrogen, and sulfur. The functional groups—carboxyl and hydroxyl—are responsible for alkali solubility, and the carboxyl are present in such an amount as to lead to average equivalent weights of 200 to 300. Severe oxidative degradation results in simple water-soluble acids such as carbonic, acetic, oxalic, succinic, and the members of the benzenecarboxylic acid series. All of that series except benzoic have been definitely shown to be present as products of the low-temperature oxidation of coals. The oxidation products of the lower-rank materials are characterized by larger proportions of carbonic acid, the simpler aliphatic acids, and the lower members of the benzenecarboxylic acid series, and the higher-rank materials by larger proportions of acids of the benzenecarboxylic series, and especially the highest member of that series, mellitic acid. These results are what would be expected if coals are looked upon as a series of structures

ranging at one end from vegetable debris of mixed aliphatic, heterocyclic, and carbocyclic structure, to graphite, the completely condensed carbocyclic structure, at the other. The larger proportion of linear structures and of oxygen-containing rings in the lower-rank materials would be expected to lead to greater yields of the simple aliphatic acids, and, conversely, the higher proportion of condensed carbocyclic structures found in the higher-rank materials would be expected to furnish higher yields of acids of the benzenecarboxylic series. With a very completely condensed carbocyclic structure, such as macrocrystalline graphite, the only oxidation products expected in significant amounts would be mellitic acid and carbonic acid, and these are the only ones yet reported.¹⁰⁹

109 There is a certain analogy between hydrogenolysis of coal and oxidative degradation, in that the yield of hydrocarbons of moderate molecular weight reaches a maximum with carbonaceous materials of intermediate rank. No hydrogenolysis product analogous to mellitic acid, however, has yet been obtained, the high-rank materials yielding methane, the analog of carbon dioxide, exclusively. At the lower end of the series the results of hydrogenolysis are obscured by the high temperatures required compared with oxidation, with consequent rapid internal structural changes. Cellulose, for example, on oxidation with alkaline permanganate at 100° C yields nothing more complex than two carbon atom structures, whereas, on hydrogenolysis at 430° C, molecules similar to those obtained from bituminous coals, probably containing ten to thirty carbon atoms, are formed. Rapid internal changes are, however, known to take place in cellulose at 200° C and above with the formation of cyclic structures.

CHAPTER 10

CHEMICAL CONSTITUTION OF COAL: AS DETERMINED BY REDUCTION REACTIONS

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With few exceptions the literature concerned with the reduction of coal has resulted from investigations dealing with the development of the high-pressure catalytic hydrogenation of coal for technical purposes. The consequence of this situation has been the accumulation of considerable data on the course of the reactions and the nature of the products when coal is treated by processes involving a combination of hydrogenation and thermal decomposition. It is the object here to present from this literature only such data as are useful in elucidating the chemical constitution of coal.

THE CHEMICAL NATURE OF THE REDUCTION PRODUCTS OF COAL, A HISTORICAL REVIEW

In 1870, Berthelot¹ published a treatise on the reducing action of strong hydriodic acid on various classes of carbon compounds and described, among others, the products resulting from the reduction of coal, wood, sugar char, and a bitumen resulting from the pyrolysis of benzene. A coal described only as yielding 4 to 5 percent of tar on distillation was treated with 100 parts of concentrated hydriodic acid in a closed tube at 280° C for 24 hours.

¹ Berthelot, M., *Ann. chim. phys.*, **20**, 526-34 (1870).

The result was a fluid product which on distillation yielded a distillate amounting to 60 percent of the weight of the original coal and a solid bitumenlike residue amounting to 35 percent. The distillate contained small amounts of hexane and benzene and higher fractions too complex to be resolved but consisting of saturated hydrocarbons of the methane and polymethylene series. Similar results with wood, sugar char, and bitumen led Berthelot to conclude that, in spite of similarity in appearance with true carbon, coal actually consisted of definite compounds of carbon, hydrogen, and oxygen, namely, polymerization products derived from the sugar-type compounds which serve as building units for plant structures.

It remained, however, for the patent disclosures² of Bergius in 1913 to initiate widespread investigation into the reduction products of coal. Bergius disclosed that coal, when treated with hydrogen at 100 atmospheres pressure at 450° C, yielded 85 percent of its weight of soluble or liquid product which, in part, consisted of oxygen-containing substances phenolic in nature and in part of hydrocarbons of a wide boiling-point range and similar to the petroleum hydrocarbons.

² Bergius, F., *Ger. Pats.* 301,231 (1913), 299,783 (1916).

In 1917, Fischer and Tropsch³ verified Berthelot's production of petroleumlike hydrocarbons from coal by the action of hydriodic acid at 250° C and described the action of this same reagent at 200° C on several coals. At 200° C no fluid material was produced but the reaction products showed a marked increase in chloroform solubility over the original coal. The chloroform extracts were bright brown powders which softened at 100° C; they were soluble in pyridine, partially soluble in benzene, and insoluble in oxygenated solvents, and they had a much higher ratio of hydrogen to carbon than the original coals.

In 1921, Fischer and Schrader⁴ published an account of the reduction of coal by the action of molten alkali formates at temperatures above 360° C. Distillation of coal at atmospheric pressure in the presence of alkali formates gave an increased tar yield over that yielded in the absence of the formates. The tars were not characterized by any analytical data, but the fact that they were quite sensitive toward heat and oxygen was evident from the low yields obtained when the products were either not swept from the still or were swept by nitrogen containing traces of oxygen (Table I). The reaction was also carried out at high pressure in a steel autoclave using anhydrous sodium formate or a concentrated aqueous solution. The reactants were heated for 3 hours at the desired temperature, and the yield of ether-soluble material was determined (Table II). The ether-soluble materials obtained at the various temperatures were quite different; at 350° C it was a red-brown viscous mass; at 400, a greaselike solid; and

TABLE I

DISTILLATION OF BROWN COAL AND BROWN COAL (1 PART) + SODIUM FORMATE (4 PARTS) CHARGES⁴

Gas Used to Sweep out Products	Tar Yield, Percent of Pure Coal	
	Coal	Coal + Sodium Formate
None	4.6	15.6
H ₂ O(g)	6.7	27.4
H ₂	6.5	24.2
N ₂ (O ₂ -free)	7.0	23.2
N ₂ (containing O ₂)*	6.1	11.6

* Commercial nitrogen in pressure tanks.

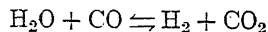
TABLE II

PRODUCTS OBTAINED FROM HEATING BROWN COAL (4 GRAMS) IN THE PRESENCE OF SODIUM FORMATE (8 GRAMS) AND WATER (8 GRAMS) IN A CLOSED AUTOCLAVE⁴

Temperature °C	Percent of Pure Coal	
	As Ether Soluble	As Residue (Organic Material)
350	28.8	32.28
400	44.9	6.64
450	7.9	12.02

at 450, a bright red-brown fluid oil. At 450° C by far the largest portion of the reaction product was gaseous.

Fischer and Schrader⁵ also demonstrated the reducing action on coal of hydrogen produced *in situ* by the water-gas reaction



but they did not characterize the products except as tars.

These earlier results have shown that the combined action of heat and reducing agents on coal gives a high yield of organic substances which range from heavy tars to

³ Fischer, F., and Tropsch, H., *Ges. Abhandl. Kenntnis Kohle*, **2**, 154-9 (1917).

⁴ Fischer, F., and Schrader, H., *Brennstoff-Chem.*, **2**, 161-73 (1921).

⁵ Fischer, F., and Schrader, H., *Brennstoff-Chem.*, **2**, 257-61 (1921).

light oils and gases, the percentage of lighter products increasing with increased severity of reaction conditions. The action is apparently one of progressive degradation of the high-molecular-weight substance comprising the coal. The exact or even the general chemical nature of the resulting fragments is the best clue to the chemical constitution of the original coal.

In 1925, Fischer and Frey⁶ reported that the hydrogenation of brown coal and of brown coal coke at 360–500° C and 70–120 atmospheres pressure yielded 30 to 40 percent distillable oils containing as much as 20 percent of phenolic material, that is, 6 to 8 percent phenolic material based on the original coal.

In the same year, Tropsch and Ter-Nedden⁷ gave the results of an analytical investigation of the oils resulting from the hydrogenation at 460° C of low-temperature coke (semicoke) from brown coal. Table III shows the yields of neutral oil, phenols, and bases, and Table IV the composition of the neutral oil fraction. Inasmuch as only a small amount of unsaturated material was present in the neutral oils, the high densities and low atomic hydrogen-to-carbon ratios indicate that the hydrocarbons were cyclic in nature, the higher-boiling fractions having a condensed polynuclear structure.

In 1926, Heyn and Dunkel⁸ published an extensive analysis of the products of the liquid-phase hydrogenation of a Lower Silesian coal. Unwashed coal dust containing 17.7 percent ash, 28.5 percent volatile matter, and an unusually high proportion of fusain was made into a paste with half of its weight of an oil from a previous

TABLE III

OIL FROM HYDROGENATION OF
BROWN COAL SEMICKE⁷

Chemical Nature	Boiling Range °C	Percent of Oil	Percent of Coke
Neutral oil	60–150	8.9	2.4
Neutral oil	150–280	38.2	10.3
Neutral oil	Over 280	17.5	4.73
Neutral oil	Residue	17.8	4.8
Phenol	181	3.2	0.86
<i>o</i> -Cresol	191	1.5	0.41
<i>m</i> -Cresol	202	1.9	0.52
Higher phenols	202–280	7.1	1.91
Higher phenols	Over 280	1.7	0.47
Bases	180–280	2.2	0.6
		100.0	27.00

TABLE IV

NEUTRAL OILS FROM HYDROGENATION OF
BROWN COAL SEMICKE⁷

Fraction No.	Boiling Range °C	Percent	D_4^{20}	Iodine No.	Carbon	Hydrogen	Atomic H/C
1	60–85	1.4	0.739		85.4	13.5	1.9
2	85–95	2.0	0.767	10.5	87.5	12.3	1.7
3	95–115	3.3				
4	115–125	2.2	0.805				
5	125–135	3.2				
6	135–145	5.2	0.830	10.0	88.2	10.9	1.5
7	145–155	3.5				
8	155–165	2.8	0.854				
9	165–175	5.3				
10	175–185	4.7	0.881				
11	185–195	7.6	0.895	13.6			
12	100 ₃₅ –115 ₃₅	17.1	0.933		90.68	9.35	1.2
13	115 ₃₅ –130 ₃₅	10.2	0.947				
14	130 ₃₅ –140 ₃₅	7.6	0.956				
15	140 ₃₅ –155 ₃₅	5.2	0.961	16.3			
16	155 ₃₅ –165 ₃₅	5.4	0.972		91.7	8.88	1.2
17	165 ₃₅ –190 ₃₅	6.8	0.993	14.5			
Residue		6.5					
				100.0			

⁶ Fischer, F., and Frey, W., *Brennstoff-Chem.*, **6**, 69–79 (1925).

⁷ Tropsch, H., and Ter-Nedden, W., *Brennstoff-Chem.*, **6**, 143–5 (1925).

⁸ Heyn, M., and Dunkel, M., *Brennstoff-Chem.*, **7**, 20–5, 81–7, 245–50 (1936).

hydrogenation, the third in a series which started with high-temperature tar as a pasting oil and thereafter used the oil from the previous hydrogenation. This paste was hydrogenated in a continuous plant of

about 15 pounds per hour capacity. The oil yield, including 3.36 percent of gasoline stripped from the gases, was 36.5 percent of the raw coal. The distribution of phenols and bases in the raw oil is given in Table V.

The combined precipitated solids were shown to be 7 percent paraffins ($C_{21}H_{44}$

the heavy fractions are significant. Simple olefins of high molecular weight are rather inactive to sulfuric acid, and the losses are probably due to the sulfuric-acid-catalyzed polymerization of high-molecular-weight conjugated olefinic systems. Although the authors made no mention of it, the losses probably occurred through the precipita-

TABLE V
DISTRIBUTION OF PHENOLS AND BASES IN OIL FROM THE HYDROGENATION OF
LOWER SILESIAN COAL⁹

Fraction	Percent of Coal Ash-Free Basis	Percentages			
		Neutral Oil	Phenols	Bases	Crystalline Precipitates
Water	6.26
Noncondensable hydrocarbons	2.60
Condensable hydrocarbons recovered from gases	4.07	100.0			
Oil:					
Boiling to 180° C	4.93	80.7	18.0	1.3	
180 to 220° C	7.14	61.2	34.2	4.6	
220 to 150° C ₁₅	2.14	81.4	14.1	4.5	
150 ₁₅ to 230° C ₁₅	8.40	90.1	4.6	3.6	1.7
230 ₁₅ to 250° C ₁₅₋₂	5.00	88.6	0.5	3.5	0.7
Nondistilling but benzene soluble	12.58	
	53.12				

to $C_{26}H_{54}$) and 93 percent aromatic hydrocarbons from which were isolated phenanthrene 40.7, carbazol 8.6, anthracene 2.2, acenaphthene 0.9, and fluorene 0.08 percent, respectively.

Table VI gives the results of the treatment of the neutral oils with concentrated sulfuric acid in order to remove unsaturated components.

The cyclic nature of the refined neutral oil is evident from the high densities and low hydrogen-to-carbon ratios; the higher fractions were undoubtedly made up of condensed-polynuclear compounds. The large losses on sulfuric acid treatment of

tion of the polymerizate as a tarry mass after sulfuric acid treatment, a phenomenon observed by other investigators.⁹

The refined neutral oils boiling up to 220° C were analyzed for aromatic content by nitration and sulfonation methods. Hydroaromatic content was estimated by dehydrogenation according to Zelinsky, followed by nitration and sulfonation (Table VII). These are minimum values, as considerable loss was entailed in their separation. The residual neutral oil in both fractions had a hydrogen-to-carbon

⁹ Weiler, J. F., unpublished. Fisher, C. H., privately communicated.

TABLE VI

SULFURIC ACID TREATMENT OF NEUTRAL OILS FROM THE HYDROGENATION OF
LOWER SILESIAN COAL⁵

		Analysis of Refined Product						
Fraction	Loss	Percent Carbon	Percent Hydrogen	Atomic H:C		D_{26}^{20}		
Condensable hydrocarbons recovered from gases	5.5	86.70	14.20	1.97		0.7617		
Boiling to 180° C	13.0	89.32	11.85	1.59		0.8238		
180 to 220° C	15.0	90.20	9.75	1.30		0.9160		
220 to 150° C ₁₅	20.0	89.50*	8.52*	8.55	1.14*	1.13	0.9779*	0.9568
150 ₁₅ to 190° C ₁₅	19.5	88.95	8.54	1.15		1.0292		
190 ₁₅ to 230° C ₁₅	48.5	88.27	7.75	1.05		1.0810		
230 ₁₅ to 250° C ₁₀₋₃	51.5	91.25	7.15	0.94		1.1143		

* Analysis of untreated fraction.

TABLE VII

AROMATIC AND HYDROAROMATIC CONTENT OF NEUTRAL OILS BOILING TO 220° C⁵

		Percent		Percent
80-145°	Benzene, Toluene, and Xylene	26.56	Cyclohexane and Methyl Derivatives	8.55
145-210°	Decalin	1.8	Tetralin	11.8

ratio of 2.1 and was, therefore, not paraffinic but of a polymethylene nature with the rings containing fewer than six carbon atoms.

The yield of phenols, if prorated between vehicle and coal by weight, would amount to a 2.5 percent yield on the ash-free coal. This figure should probably be higher since it has been shown¹⁰ that as many as seventeen successive runs are necessary to produce maximum yields of tar acids when starting with an anthracene pasting oil. Fractionation of the phenols, Table VIII, shows that phenol, the cresols,

and the xylenols, boiling at 220° C or below, made up 66 percent of the total.

The yield of bases from the hydrogenation amounted to only 0.75 percent on the ash-free coal when prorated between the vehicle and the coal. Treatment with nitrous acid resolved the bases into 20 percent primary, 5 percent secondary, and 60 percent tertiary. Aniline, the toluidines, and xylidines were identified, but no secondary amines; only small amounts of quinoline, isoquinoline, symmetrical colloidine, and quinaldine were identified from the tertiary amines.

These earlier investigations of Tropsch and Ter-Nedden and of Heyn and Dunkel, indicating that the distillable hydrogenation products of a brown coal semicoke and

¹⁰ Hirst, L. L., Hawk, C. O., Sprunk, G. C., Golden, P. L., Pinkel, I. I., Boyer, R. H., Schaeffer, J. R., Kallenberger, R. H., Hamilton, H. A., and Storch, H. H., *Ind. Eng. Chem.*, **31**, 869-77 (1939).

TABLE VIII

PHENOLIC FRACTIONS FROM HYDROGENATION
OF LOWER SILESIAN COAL⁵

Boiling Range °C	Percent of Total	Boiling Range °C	Percent of Total
179-181	10.1	205-210	5.0
181-188	10.7	210-215	6.4
188-195	11.3	215-220	5.7
195-200	9.7	220-250	15.0
200-205	7.6	250-270	4.8
		Over 270	13.7

of a bituminous coal, respectively, are almost exclusively cyclic in nature, have been confirmed for other coals by numerous later workers. In nearly all instances the distillable products exclusive of gases represented less than 50 percent of the carbon and even less of the oxygen. The nature and reaction history of the remainder of these two elements will be discussed later.

By batch hydrogenation in small autoclaves of Maria Luisa long-flame coal, Perterra¹¹ obtained an oil that contained 32 percent phenols and 8.2 percent nitrogen bases. The neutral oil boiling at 95° to 145° C contained 52 percent aromatics, 28.7 percent saturates, and 7.3 percent unsaturates. The tar acids included phenol, pyrocatechol, and *o*- and *m*-cresol; the tar bases contained pyridine and 2,4-dimethylpyridine. Most of the bases, 68.6 percent, were tertiary; 3.8 percent were primary and 27.6 percent secondary.

The work of British investigators shows that hydrogenation of Beamshaw,¹² Parkgate,¹² Mitchel Main,¹³ and Lanarkshire¹⁴ coals yields considerable quantities of tar

acids, tar bases, and aromatic oils boiling from room temperature to 360° C. Similar results have been reported for Russian brown coal,¹⁵ Japanese,¹⁵ Chinese,¹⁵ and Canadian coals.¹⁶

Storch and coworkers¹⁷ at the U. S. Bureau of Mines have published a characterization of the hydrogenation products of four United States high-volatile bituminous coals. The hydrogenations were carried out in a continuous plant, the data being collected on the products from the last three of eight to fourteen successive runs in order to eliminate the effect of the original coal-tar pasting oil. The catalyst was 0.5 percent stannous sulfide and 0.5 percent molybdenum trioxide; the temperature was 430° C; the contact time, 2 hours; and hydrogen pressure, 4,000 pounds per square inch. The oils distilling to 330° C were almost completely cyclic in nature and contained approximately 60 percent of the carbon of the original coals. The data are summarized in Table IX.

Evidence for a condensed-polynuclear structure for the high-boiling fractions from coal hydrogenation products is found in the claims of several patents to the isolation of many polynuclear aromatic compounds of high molecular weight. Products of this kind include pyrene,^{18, 19, 20, 21, 22, 23} chrysene,^{19, 20, 22} re-

¹⁵ D'yakova, M. K. and Lozovoi, A. V., *Compt. rend. acad. sci., U.R.S.S.*, **2**, 257-8 (1935). Uchida, M., *J. Fuel Soc. Japan*, **14**, 38-44 (1935). Hsiao, C. C. and Lo, C. L., *J. Chem. Eng. China*, **4**, 248-54 (1937).

¹⁶ Warren, T. E., and Bowles, K. W., *Can. Dept. Mines, Mines Branch, Rept.* **737-3**, 11-31 (1933).

¹⁷ Hirst, L. L., Storch, H. H., Fisher, C. H., and Sprunk, G. C., *Ind. Eng. Chem.*, **32**, 864-71 (1940).

¹⁸ Pier, M., and Schoenemann, K., *Ger. Pat.* 639,240 (1936).

¹⁹ Pier, M., and Schoenemann, K., *Ger. Pat.* 654,082 (1937).

²⁰ I. G. Farbenindustrie A.-G., *Brit. Pat.* 435,254 (1935).

¹¹ Perterra, J. M., *Anales soc. españ. fis. quim.*, **28**, 792-806 (1930), **30**, 792-3 (1932).

¹² Horton, L., Williams, F. A., and King, J. G., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper* **42** (1935), 58 pp.

¹³ Bakes, W. E., *ibid.*, **37**, 157-210 (1933).

¹⁴ *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March* **31**, 1930, pp. 105-6.

TABLE IX

HYDROGENATION PRODUCTS FROM HIGH-VOLATILE U. S. BITUMINOUS COALS—
PERCENTAGE OF DRY, ASH-FREE COAL¹⁷

Coal	Oil	Tar Bases	Tar Acid		Neutral Oils		
	Distilling	Distilling	Distilling		Distilling to 330° C		
	to 330° C	to 330° C	to 235° C	to 330° C	Olefins	Aro- matics	Saturates (Cyclic)*
Pittsburgh, Pa.	65.2	2.8	7.6	3.5	3.1	36.7	11.5
No. 6, Illinois	52.4	1.6	4.4	7.0	3.5	22.6	12.7
McKay, Washington	61.4	3.2	4.9	8.1	5.8	22.0	17.4
Mary Lee, Alabama	55.0	2.3	3.9	3.5	3.3	29.0	13.0

* Approximately 70 percent cyclic.

tene,²⁰ fluoranthene,²¹ carbazole,²¹ methyl- and dimethylpyrenes,²¹ 1,12-benzoperylene,^{21, 23, 24} coronene,^{21, 23, 24} picene,²¹ fluorene,²⁴ methyl- and dimethylantracene,²⁵ methyl- and dimethylnaphthalene,²⁵ and methylfluorene.²⁵ The various patents describe much the same process. The crude high-boiling fractions from destructive hydrogenation of coal are first freed of heavy paraffinic material by cooling after addition of a selective solvent for nonparaffinic substances, for example, methyl formate, and then freed of asphaltic substances by an adsorbent or through precipitation when the product is highly diluted with low-boiling saturated hydrocarbons. The refined oil is then subjected to dehydrogenation at temperatures from 300 to 700° C over various catalysts. The polynuclear aromatic hydrocarbons of four or more rings are described as resulting from dehydrogenation treatment at temperatures of 500° C or above. At these temperatures considerable rearrangement takes place in the dehy-

drogenation of hydrides of polynuclear hydrocarbons so that it cannot be said that the hydrides of the recovered aromatics were necessarily present. However, it seems safe to conclude that polynuclear hydrocarbons of the same general molecular magnitude were present.

Biggs and Weiler²⁶ described liquid and solid resinous products obtained from coal under hydrogenation conditions which were designed to avoid thermal cracking as far as possible. The extract and residue from the benzene extraction of a Pittsburgh Seam coal at 260° C were hydrogenated separately. Hydrogenation was carried out in a rocking-type autoclave at 350° C with 10 percent of Adkins copper chromite catalyst and no vehicle. After a 12- to 16-hour heating period, the reaction product was freed of petroleum-ether-soluble material and the residue was returned to the autoclave with fresh catalyst for further hydrogenation. This cycle was repeated several times. The accumulated petroleum-ether-soluble material was then hydrogenated over Raney nickel at 220° C with cyclohexane as a vehicle. From the composition, refractive index, and molecular weights (Table XVIII), it was concluded that the products boiling above 200° C

²¹ I. G. Farbenindustrie A.-G., Brit. Pat. 470,338 (1936).

²² Pier, M., and Schoenemann, K., Ger. Pat. 655,103 (1938).

²³ I. G. Farbenindustrie A.-G., Brit. Pat. 497,089 (1937).

²⁴ Scholl, R., and Meyer, K., *Ber.*, **71**, 407 (1938).

²⁵ Pier, M., and Schoenemann, K., Ger. Pat. 659,878 (1938).

²⁶ Biggs, B. S., and Weiler, J. F., *J. Am. Chem. Soc.*, **59**, 369-72 (1937).

from both the extract and residue were chiefly condensed polycyclic hydroaromatic substances.

LeClaire²⁷ examined the nature of the "oils" resulting from four bituminous coals, Pocahontas No. 3 Seam, High Splint Seam, Pittsburgh Seam, and Illinois No. 6 Seam, when hydrogenated according to the procedure of Biggs and Weiler.²⁸ On the basis of physical properties (Table X) it was concluded that the oils were essentially condensed polycyclic hydroaromatic hydrocarbons with occasional paraffinic side chains. Figure 1 shows a plot of molecular volume against molecular weight for paraffinic and perhydroaromatic hydrocarbons and the hydrogenation products from the

four coals. A method²⁸ of determining the nature of the saturated hydrocarbons in petroleum oils based on the relation between specific refraction and molecular weight of different types of hydrocarbons was applied to the oils (Fig. 2). Figure 2 shows that as many as six or seven condensed rings were present in the components of the higher fractions. It is suggestive that in all the fractions the components have roughly the same number of carbon atoms in paraffinic side chains; that is, all the points lie roughly the same distance to the right of the points representing the first member of the homologous series to which they most nearly conform. This distance represents approximately

²⁷ LeClaire, C. D., *J. Am. Chem. Soc.*, **63**, 343-51 (1941).

²⁸ Vlughter, J. C., Waterman, H. I., and van Westen, H. A., *J. Inst. Petroleum Tech.*, **21**, 661-76, 701-8 (1935).

TABLE X

PROPERTIES OF THE PETROLEUM-ETHER-SOLUBLE PRODUCTS FROM THE HYDROGENATION OF FOUR BITUMINOUS COALS: (1) POCAHONTAS NO. 3 SEAM, (2) PITTSBURGH SEAM, (3) HIGH SPLINT SEAM, AND (4) ILLINOIS NO. 6 SEAM²⁷

Approximate Boiling Range	Source	C percent	H percent	Molecular Weight	Density	Index of Refraction	$\frac{n_F - n_C}{d}$	Aniline Point
100-140 mm	1	84.9	13.1	208	0.880	1.4772	0.00979	60.3
to	2	85.1	13.0	209	0.875	1.4742	0.00978	61.0
165 mm	3	86.3	12.6	198	0.877	1.4742	0.00952	59.6
	4	86.2	13.0	189	0.875	1.4744	0.00979	60.6
165 mm	1							
to	2							
205 mm	3	86.9	12.6	254	0.917	1.4941	0.00983	70.4
	4	86.5	12.7	253	0.921	1.4963	0.00959	71.5
205 mm	1	87.0	12.0	306	0.967	1.5171	0.00958	79.0
to	2	86.8	12.3	320	0.962	1.5146	0.00970	77.8
265 mm	3	86.3	11.8	316	0.956	1.5118	0.00967	79.5
	4	86.8	12.0	323	0.958	1.5132	0.01032	80.0
265 mm	1	87.9	11.4	422	1.003	1.5372	0.01017	85.0
to	2	382	1.000	1.5388	0.01066	62.8
310 mm	3	87.4	11.7	420	0.998	1.5370	0.01013	82.5
	4	87.2	11.8	424	1.000	1.5358	0.01045	88.0

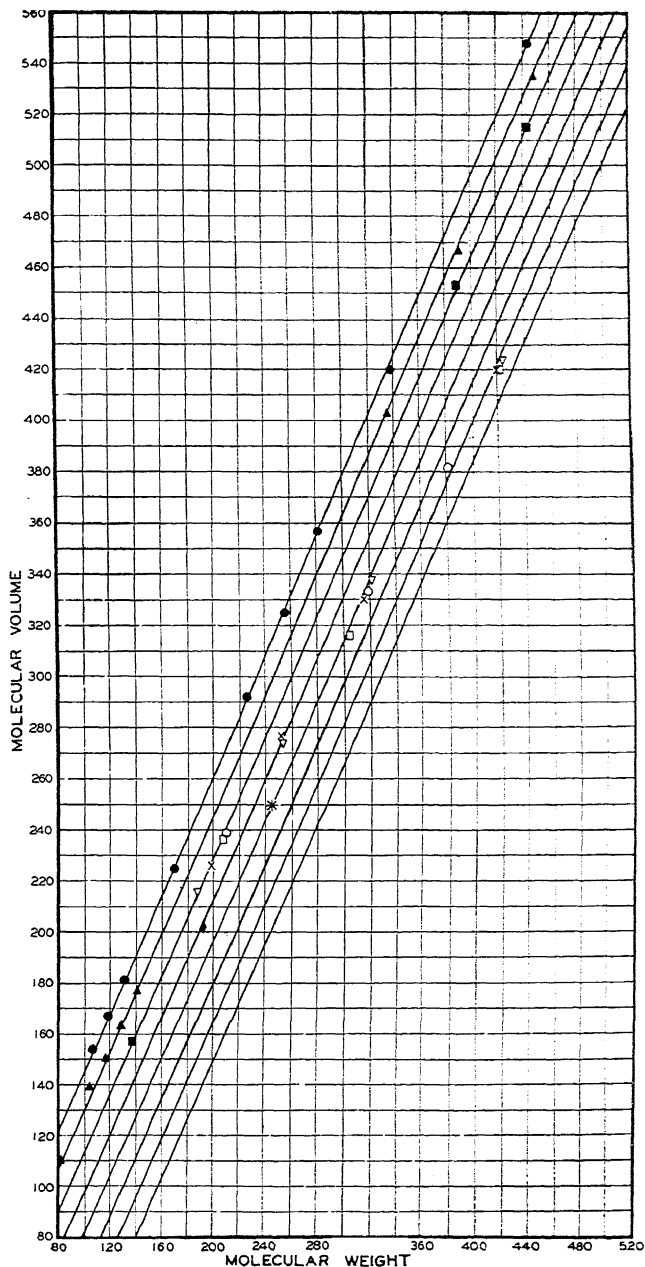


FIG. 1. Molecular weight versus molecular volume of paraffinic and perhydroaromatic hydrocarbons and derivatives including the hydrogenation products from four coals: ²⁷ paraffins, derivatives, ▲; decalin derivatives, ■; perhydrophenanthrene, ◆; perhydrochrysene, *; Pocahontas No. 3, □; High Splint, ×; Pittsburgh, ○; Illinois No. 6, ▽.

sixty molecular weight units or four CH_2 groups. This fact may mean that the degradation resulting in all these various sized units has been the result of the breaking of the same type of linkage, leaving

the oxygenated compounds contained therein were neutral and not phenolic. The authors regarded the boghead coal as polycyclic carboxylic acids formed by the polymerization of unsaturated fatty acids which

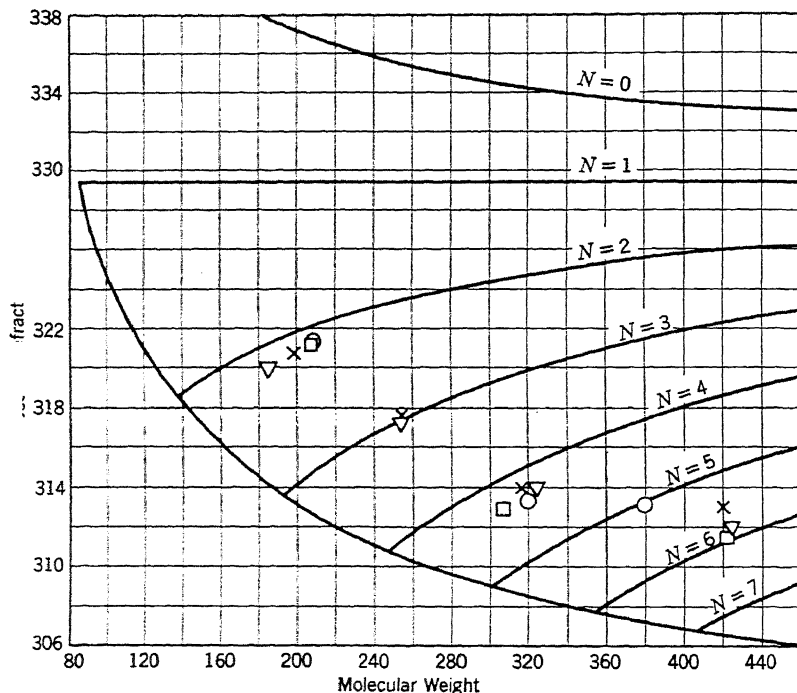


FIG. 2. Molecular weight versus specific refraction of paraffins and paraffin side-chain homologs of linearly or angularly condensed perhydroaromatic hydrocarbons.²⁹ The points for such hydrocarbons lie on the line $n = 0$, $n = 1$, $n = 2$, etc., where n is the number of rings in the molecule. The saturated hydrogenation products of the four coals are represented as follows:

Pocahontas No. 3, □.
High Splint, x.

Pittsburgh, O.
Illinois No. 6, ▽.

each unit with the same side chain or chains.

Somewhat different from the results obtained with other types of coal are those reported by Stadnikoff and Kaschtanov²⁹ for the hydrogenation of a Siberian boghead coal. Although the liquid products were largely saturated cyclic hydrocarbons,

were contained in the fats from algae. The neutral oxygenated compounds were regarded as ketones formed by the loss of carbon dioxide from the polycarboxylic acids.

The analytical investigations so far described show that coals of many different sources when subjected to the action of heat and reducing agents, in particular the process of high-pressure catalytic hydro-

²⁹ Stadnikoff, G., and Kaschtanov, L., *Brennstoff-Chem.*, **10**, 417-9 (1929).

genation, yield approximately half of their carbon as distillable carbocyclic organic compounds, mostly hydrocarbons but containing significant amounts of oxygenated compounds.

The interpretation of these data on the reduction products of coal in terms of the chemical constitution of coal requires consideration of three important questions, namely: (1) what account must be taken of the fact that these reduction products were derived from an apparently heterogeneous starting material, (2) what account must be taken of such recognized differences in coals as are displayed by coals of different rank, (3) to what extent can the described reduction products be considered as primary, and what deductions can be made concerning the carbon, hydrogen, and oxygen appearing as simple fission products, e.g., water, carbon dioxide, and gaseous hydrocarbons, and as reduction products not amenable to satisfactory analytical investigation, e.g., nondistillable pitches and insoluble residues; in brief, what is the mechanism of the formation of reduction products from coal.

THE PHYSICAL AND CHEMICAL COMPONENTS OF COAL, THEIR BEHAVIOR UPON REDUCTION

Physical Components. The petrographic constituents of coal (see Chapter 3) are recognized as the physical components of the organic or "pure coal" part of coal. The behavior of these banded constituents of coal during liquefaction by hydrogenation varies with the constituents. It is generally reported^{12, 30, 31, 32, 33} that fusain

is liquefied with difficulty or not at all by high-pressure hydrogenation. Wright and Gauger³⁰ concluded from their work on American coals that all banded constituents other than fusain were completely liquefied but later reported³⁴ that another constituent, probably opaque attritus, offered some resistance to hydrogenation. Fisher and Eisner³⁵ also showed that some constituent of a Pittsburgh Seam coal other than fusain is difficult to hydrogenate. This agrees with the results of English investigators^{12, 30, 32} who found that, with one exception, the six vitrains and clarains (which contain much anthraxylon) they studied gave fair liquefaction yields, whereas two durains (attritus) gave poor yields. It is also in agreement with workers^{13, 36} who hydrogenated bright (principally anthraxylon) and dull (attrital) coals and found the bright coals more reactive than the dull coals. On the other hand, other workers³⁷ have claimed that durain is well suited for hydrogenation. The discrepancies in these claims are traceable to the heterogeneous and variable nature of durains. Whereas such constituents of durain as spores and resins are easily hydrogenated,³³ opaque matter is resistant and yields would be expected to vary widely as the ratio of these constituents varied.

³² Graham, J. I., and Skinner, D. G., *J. Soc. Chem. Ind.*, **48**, 129-36T (1929).

³³ Francis, W., *J. Inst. Fuel*, **6**, 301-13 (1933).

³⁴ Wright, C. C., and Gauger, A. W., *Am. Mining Congress Yearbook*, **1937**, 381-3.

³⁵ Fisher, C. H., and Eisner, A., *Ind. Eng. Chem.*, **29**, 1371-6 (1937).

³⁶ Fischer, F., Peters, K., and Cremer, W., *Fuel*, **12**, 390-4 (1933). Gordon, K., *Trans. Inst. Mining Engrs. (London)*, **82**, Pt. 4, 348-63 (1933). Hovers, T., Koopmans, H., and Pieters, H. A. J., *Fuel*, **15**, 233-4 (1936). Petrick, A. J., Gaigher, B., and Groenewoud, P., *J. Chem. Met. Mining Soc. S. Africa*, **38**, 122-44, 334-7 (1937).

³⁷ Lehmann, K., and Hoffmann, E., *Glückauf*, **67**, 1-17 (1931). Streven, J. L., *J. Inst. Fuel*, **4**, 317-39 (1932); *Colliery Guardian*, **142**, 572-6, 667-8 (1931).

³⁰ Thiessen, R., and Francis, W., *U. S. Bur. Mines, Tech. Paper* **446** (1929), 27 pp.; *Fuel*, **8**, 385-405 (1929). Wright, C. C., and Gauger, A. W., *Bituminous Coal Research, Inc., Tech. Rept.* **2** (1936), 25 pp. Legrand, C., and Simonovitch, M., *Fuel*, **17**, 145-60 (1938).

³¹ Shatwell, H. G., and Graham, J. I., *Fuel*, **4**, 25-30, 75-81, 127-31 (1925).

Erasmus³⁸ claimed that durains of high hydrogen content are particularly suitable for hydrogenation. Spores, one durain component of high hydrogen content, have been liquefied in excellent yield by hydrogenation.³⁹

The most extensive work on the hydrogenation of the petrographic constituents of coal has been that of the U. S. Bureau of Mines. The liquefaction yields of many samples of fusain,⁴⁰ anthraxylon,^{41, 42} and attrital constituents^{42, 42} were determined. The hydrogenation was carried out in a small-batch autoclave; the charge consisted of 100 grams of coal substance, 100 grams of tetrahydronaphthalene as vehicle, and 1 gram of stannous sulfide as catalyst; the hydrogen pressure was 1,000 pounds per square inch at room temperature; the reaction time was 3 hours. The liquefaction yields were reported as 100 minus the benzene-insoluble residue on the dry, ash-free basis. The pitches described in the tables were the distillation residues of the liquefied products distilled to 215° C to remove vehicle solvent.

The fusains (Table XI) were not entirely inert, the liquefaction yield increasing with increased oxygen and hydrogen contents. It was noted that liquefaction proceeded readily to a certain point and then became difficult, indicating two main

³⁸ Erasmus, Paul. *Über die Bildung und den chemischen Bau der Kohlen*, Ferdinand Enke, Stuttgart, 1938, pp. 1-6.

³⁹ Fisher, C. H., *Ind. Eng. Chem., Anal. Ed.*, **10**, 374-8 (1938).

⁴⁰ Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., and Storch, H. H., *Ind. Eng. Chem.*, **31**, 190-5 (1939).

⁴¹ Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., and Storch, H. H., *Fuel*, **18**, 196-203 (1939).

⁴² Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., and Storch, H. H., *Ind. Eng. Chem.*, **31**, 1155-61 (1939).

⁴³ Fisher, C. H., Sprunk, G. C., Eisner, A., Clarke, L., and Storch, H. H., *Fuel*, **18**, 132-41 (1939).

TABLE XI

LIQUEFACTION YIELDS FROM VARIOUS FUSAINS⁴⁰

Sample No.	Analysis				Hydrogenation Temperature °C	Liquefaction Yield percent
	Carbon percent	Hydrogen percent	Oxygen percent	C/H		
1	92.6	2.8	3.7	33.1	400	11.0
2	93.0	2.9	0.6	32.1	430	11.7
3	92.6	3.0	0.3	30.9	430	19.5
4	89.5	3.1	6.4	28.9	400	26.3
5	93.5	3.3	2.4	28.3	430	10.4
6	92.0	3.3	3.7	27.9	430	15.7
7	88.1	3.5	5.8	25.2	430	24.4
	Bruceston coal				400	89.4
	Bruceston coal				415	92.9

constituents differing greatly in amenability to liquefaction. The insoluble residues were characterized by a high carbon content and high carbon-to-hydrogen ratio as compared to the liquefied pitches (Table XIV). According to the authors the data are suggestive of the conclusions of Seyler⁴⁴ that fusain is composed of two fundamentally different components, "fusinite" and "vitrinite." Fusinite, the main component, is the component resistant to hydrogenation, while vitrinite, similar to vitrain (anthraxylon) in reactivity and volatile-matter content, is the component liquefied by hydrogenation.

From Table XII it is apparent that anthraxylons are much more readily liquefied than fusains, being, regardless of rank, almost completely liquefied under these conditions.

Of the various components of attrital matter (Table XIII) the resins and translucent portions are readily liquefied. The opaque matter, however, shows appreciable insoluble residues. These insoluble residues also are characterized by a high carbon content and high carbon-to-hydrogen ratio

⁴⁴ Seyler, C. A., *Colliery Guardian*, **155**, 990-4, 1046-8, 1087-9, 1187-9, 1231-3 (1937).

TABLE XII
LIQUEFACTION YIELDS FROM VARIOUS
ANTHRAXYLONS ^{41, 42}

Sample No.	Analysis				Hydrogenation Temperature °C	Liquefaction Yield percent
	Carbon percent	Hydrogen percent	Oxygen percent	C/H		
1	81.5	5.4	9.7	15.1	430	93.3
2	81.5	5.6	8.3	14.6	430	98.0
3	81.7	5.2	10.4	15.7	430	97.8
4	83.0	5.5	8.2	15.1	430	98.3
5	83.5	5.7	8.7	14.6	430	90.4
6	84.5	5.5	7.3	15.4	400	98.3
7	85.3	5.4	6.9	15.8	430	97.8
8	85.9	5.4	6.1	15.9	430	98.2
9	86.1	5.3	6.4	16.2	430	95.8
10	87.8	5.3	4.4	16.6	430	97.2
11	89.9	4.8	2.9	18.7	415	95.4

as compared to the liquefied pitches (Table XVI) but have much lower carbon contents and carbon-to-hydrogen ratios than the fusain residues.

The composition of the pitches (Tables XIV, XV, XVI) from the various samples of the same petrographic constituent varies but little. There appears to be a tendency for the pitches from the samples of higher rank to have a lower oxygen content and higher carbon-to-hydrogen ratio. Statis-

tical analysis of the data indicates that more consistent data or a larger number of observations is desirable to establish definitely that such a relationship exists. The average composition of the pitches from the various constituents (Table XVII) with the exception of those from the spores and resins is nearly the same. The spores and resins have a definitely lower carbon-to-hydrogen ratio.

The available data on the hydrogenation of the petrographic constituents indicate that, where the resin and spore contents of the coals have not been high, conclusions drawn from the reduction products of the whole coal apply about equally well to the component petrographic constituents, that is, the part thereof that has been converted into the products in question. It is almost certain that differences in some details of chemical constitution exist between the various petrographic constituents. Such differences may or may not account for differences in liquefaction yields inasmuch as the hydrogenation *versus* liquefaction yield parameter is essentially a rate factor in which a solution process is involved, wherefore physical differences might also

TABLE XIII
LIQUEFACTION YIELDS FROM VARIOUS ATTRITAL CONSTITUENTS ^{42, 43}

Sample No.	Analysis				Hydrogenation Temperature °C	Liquefaction Yield percent
	Carbon percent	Hydrogen percent	Oxygen percent	C/H		
1. Opaque attritus	88.0	4.8	5.1	18.3	422	65.2
2. Opaque attritus	85.4	4.7	8.1	18.2	430	59.8
3. Opaque attritus	86.9	4.4	7.0	19.8	415	78.4
4. Opaque attritus	85.6	5.3	6.1	16.1	400	85.6
5. Opaque attritus	87.5	5.5	5.1	15.9	430	75.5
6. Translucent attritus	85.5	6.0	5.0	14.3	430	90.0
7. Translucent attritus	83.0	5.8	8.8	14.3	430	93.0
8. Translucent attritus	79.3	6.3	11.0	12.6	430	90.0
9. Spore-rich cannel coal	83.3	8.4	3.9	9.9	430	92.6
10. Spores	80.6	7.6	9.4	10.6	400	96.0
11. Resins	83.6	10.2	5.7	8.2	430	99.8

TABLE XIV

COMPOSITION OF PITCHES AND INSOLUBLE RESIDUES FROM LIQUEFACTION OF FUSAIN⁴³

Sample No.*	Pitches				Insoluble Residues			
	Carbon percent	Hydrogen percent	Oxygen percent	C/H	Carbon percent	Hydrogen percent	Oxygen percent	C/H
1	89.0	7.3	2.5	12.2	93.2	2.6	3.7	35.6
2	90.3	6.8	1.7	13.3	93.6	2.6	3.0	36.0
3	89.4	8.1	1.6	11.0	94.3	2.6	2.3	36.3
4	91.6	7.6	0.4	12.1	95.4	2.9	1.1	32.9
5	91.5	6.9	0.6	13.3	94.1	3.1	2.1	30.3
6	89.9	7.7	1.4	11.7	94.2	3.0	2.0	31.4
7	88.8	7.5	2.6	11.8	91.7	3.3	4.1	27.8
Coal	88.7	7.8	2.4	13.0
Coal	89.7	7.2	1.5	12.4	92.0	4.9	0.4	18.8

* These numbers refer to the same samples as in Table XI.

TABLE XV

COMPOSITION OF PITCHES AND INSOLUBLE RESIDUES FROM LIQUEFACTION OF ANTHRAXYLONS^{42, 43}

Sample No.*	Pitches			C/H	Residues
	Carbon percent	Hydrogen percent	Oxygen percent		
1	90.0	6.9	1.3	13.0	Ash content so high that estimation of the composition of the organic matter was entirely unsatisfactory
2	89.1	6.9	2.0	12.9	
3	90.7	6.9	1.0	13.1	
4	89.7	6.8	1.5	13.2	
5	90.1	6.5	1.9	13.8	
6	88.3	6.8	2.9	13.0	
7	90.2	6.7	1.6	13.5	
8	90.0	6.6	1.6	13.6	
9	90.3	6.5	1.6	13.9	
10	90.7	6.3	1.1	14.4	
11	91.7	6.1	0.4	15.0	

* These numbers refer to the same samples as in Table XII.

be expected to play some part. Certainly the spores and resins are less highly condensed polynuclear systems than the other constituents of coal, and this may account for the greater ease with which they are liquefied.

Chemical Components. Solvent extraction serves to separate coal roughly into various components. (Cf. Chapter 19.)

Thus, a coal may be separated into a benzene soluble-alkali insoluble or "bitumen fraction," a benzene insoluble-alkali soluble or "humic" fraction, and an insoluble residue.

The extract and residue from the extraction of a Pittsburgh Seam coal with benzene under pressure at a temperature of 260° C have been used in hydrogenation studies^{26, 45, 46} of the chemical constitution of coal. The benzene extract, 14.5 percent of the weight of the coal, was divided into three fractions: (1) that portion soluble in a large excess of petroleum ether (16.2 percent); (2) that portion insoluble in petroleum ether but soluble in ethyl ether (50.4 percent); and (3) that portion insoluble in ethyl ether (33.4 percent). High-pressure catalytic hydrogenation at 425° C yielded⁴⁵ from both fraction 2 and fraction 3 about 50 percent of the original carbon as steam-distillable oils of almost identical composition. The chemical properties and physical constants of various fractions from these oils indicated that except for the low-boiling materials, which contained

⁴⁵ Biggs, B. S., *J. Am. Chem. Soc.*, **58**, 484-7 (1936).⁴⁶ Biggs, B. S., *ibid.*, **58**, 1020-4 (1936).

TABLE XVI

COMPOSITION OF PITCHES AND INSOLUBLE RESIDUES FROM THE LIQUEFACTION OF ATTRITAL MATTER^{42, 43}

Sample No. *	Pitches				Residues			
	Car- bon percent	Hydro- gen percent	Oxy- gen percent	C/H	Car- bon percent	Hydro- gen percent	Oxy- gen percent	C/H
1. Opaque attritus	90.4	6.4	1.6	14.1	88.7	4.0	5.3	22.2
2. Opaque attritus	90.9	6.4	1.5	14.2	90.5	3.9	3.5	23.2
3. Opaque attritus	92.1	6.4	0.7	14.4	89.1	4.0	5.2	22.3
4. Opaque attritus	88.7	7.0	2.4	12.7	89.5	4.3	4.2	20.8
5. Opaque attritus	90.1	7.1	1.4	12.7	89.9	3.9	4.2	23.1
6. Translucent attritus	90.2	6.6	0.9	13.7	86.5	3.9	7.1	22.2
7. Translucent attritus	89.9	6.5	1.5	13.8	89.3	3.9	4.2	22.9
8. Translucent attritus	89.3	7.5	1.5	11.9	67.7	6.2	23.6	10.9
9. Spore-rich cannel coal	86.4	9.8	2.0	8.9	95.4	3.2	...	29.8
10. Spores	87.2	8.7	2.7	10.0	83.9	7.0	6.0	12.0
11. Resins	88.7	9.8	0.9	9.1

* These numbers refer to the same samples as in Table XIII.

TABLE XVII

AVERAGE COMPOSITION OF FUSAIN PITCHES, ANTHRAXYLON PITCHES, ATTRITUS PITCHES, AND PITCHES FROM RESINS AND SPORES^{41, 42, 43}

Source of Pitch	Carbon percent	Hydrogen percent	Oxygen percent	C/H
Fusains	90.1	7.4	1.5	12.2
Anthraxylons	90.1	6.6	1.5	13.1
Opaque attritus	90.3	6.7	1.5	13.6
Translucent attritus	89.8	6.9	1.3	13.6
Resins and spores	87.4	9.4	1.9	9.3

some aliphatic compounds, the oils were made up almost entirely of wholly or partially hydrogenated aromatic compounds. Dehydrogenation of these oils over platinumized charcoal yielded monocyclic, bicyclic, and higher aromatic hydrocarbons. The benzene-insoluble residue was then compared⁴⁶ with the extract. It was found that hydrogenation of the residue at 350° C yielded a benzene-soluble material which could be fractionated into petroleum-ether-soluble, ethyl-ether-soluble, and ethyl-ether-insoluble fractions which corresponded (in every respect) to similar fractions from the

original benzene extract of the coal. Fischer, Peters, and Cremer³⁹ had previously shown that a Pittsburgh coal which contained 7.5 percent bitumen extractible with benzene gave 35 percent of benzene-soluble "pseudobitumen" when treated with benzene at 180° C for 140 hours under 180 atmospheres hydrogen pressure provided that the coal had been reduced to a particle size of approximately 1 micron before treatment. This pseudobitumen was found to be an effective caking agent similar to the natural oily bitumen.

Biggs and Weiler²⁶ carried the comparison of benzene extract and residue still further and found that both extract and residue yielded approximately 80 percent of their carbon as cyclohexane-soluble oils when subjected to repeated successive hydrogenation and cyclohexane extraction. The hydrogenations were carried out at 350° C with Adkins copper chromite catalyst. The soluble oils were further hydrogenated over Raney nickel catalyst at 220° to achieve further saturation and were then

fractionated and characterized by molecular weights, boiling points, refractive indices, and ratio of hydrogen to carbon atoms (see Table XVIII, which also shows the physical constants of some known hydroaromatic compounds). In addition, hydroxyl content was estimated by acetylation.

The composition of the oils from the two sources was very similar, and, though the oil from the residue showed somewhat more material of higher boiling range, the difference in distribution of material between the various fractions was not suf-

ficient to suggest a marked difference in the size or stability of the molecules comprising the extract and residue (Fig. 3). This behavior supports the viewpoint that the benzene-insoluble and -soluble parts of this coal differ more in the size of polymeric aggregates than in essential chemical structure.⁴⁷ The similarity in composition of the different fractions and known polynuclear hydroaromatic hydrocarbons of corresponding boiling point and molecular weight is additional evidence for a poly-

⁴⁷ Howard, H. C., *J. Phys. Chem.*, **40**, 1103-12 (1936).

TABLE XVIII

COMPARISON OF THE PROPERTIES OF SOME KNOWN HYDROAROMATIC COMPOUNDS WITH VARIOUS FRACTIONS OF THE HYDROGENATION PRODUCTS OF THE RESIDUE (R) AND EXTRACT (E) FROM THE BENZENE PRESSURE EXTRACTION OF A BITUMINOUS COAL²⁶

Fraction No.*	Grams	Mole Percent	Weight Percent	Initial Atmospheric Boiling Point °C	n_D^{25}	Molecular Weights †		Empirical Formulas			
						Catechol	Diphenyl	C	H	OH	H/C
R ₁	3.0	6.9	2.2	190	1.467	122	128	8.7	15.6	0.34	1.83
R ₂	5.4	11.1	4.0	205	1.482	146	144	10.0	17.1	0.33	1.74
R ₃	2.5	4.2	1.9	230	1.494	175	177	12.5	20.6	0.32	1.67
R ₄	5.5	8.2	4.1	262	1.509	195	198	14.1	22.5	0.29	1.61
R ₅	2.5	3.4	1.9	315	1.524	198	218	15.6	23.8	0.26	1.54
R ₆	15.9	18.6	11.8	326	1.540	244	252	18.2	27.2	0.30	1.51
R ₇	17.9	15.6	13.3	395	1.563	330	338	24.6	33.2	0.42	1.37
R ₈	16.4	10.8	12.1	450	1.593	405	448	33	44	0.42	1.35
R ₉	51.6	21.2	38.2	520	720	53	64	0.75	1.21
Loss	14.3	10.6
E ₁	10.8	26.7	13.0	220	1.498	165	170	12	19.3	0.34	1.63
E ₂	7.7	14.5	9.2	315	1.533	218	224	16	24.0	0.30	1.52
E ₃	16.5	23.6	19.6	335	1.567	275	295	21.5	29.7	0.36	1.39
E ₄	3.0	3.5	3.6	440	1.594	377	357	26.4	35.9	0.29	1.34
E ₅	10.3	10.2	12.2	460	1.613	384	427	31.4	38.1	0.38	1.23
E ₆	35.7	21.5	42.5
Deca(per)hydronaphthalene				185	1.468	138		10	18	1.80
Tetradeca(per)hydrophenanthrene				(250) ‡	1.499	192		14	24	1.71
Dodecahydrophenanthrene				268	1.508	190		14	22	1.57
Octadeca(per)hydrochrysene				360	1.521	246		18	30	1.68
Hexadecahydrochrysene				(380)	1.541	244		18	28	1.55
Octadeca(per)hydrotriphylene				...	1.518(n_D^{25})	246		18	30	1.68
Hypothetical compound with 7 rings				>400	320		24	34	1.41

* R₁-R₅ are from the refractionation of a fraction taken off at atmospheric pressure. R₉ is the residue remaining in the still. E₆, nondistillable in the conventional apparatus, was further distilled in a molecular still but with partial decomposition so that analytical data for this fraction are not available.

† Reproducible to 1 part in 10.

‡ Atmospheric boiling points given in parentheses are estimated from values given for lower pressures.

nuclear cyclic structure for the hydrogenation products of coal.

Fischer and Schrader,⁴ while studying the reduction of coal by aqueous sodium

bitumen-poor coal. Furthermore, the composition of the oils was almost identical.

The hydrogenation of the bitumen and humic acids extracted from Aleksandriiskii

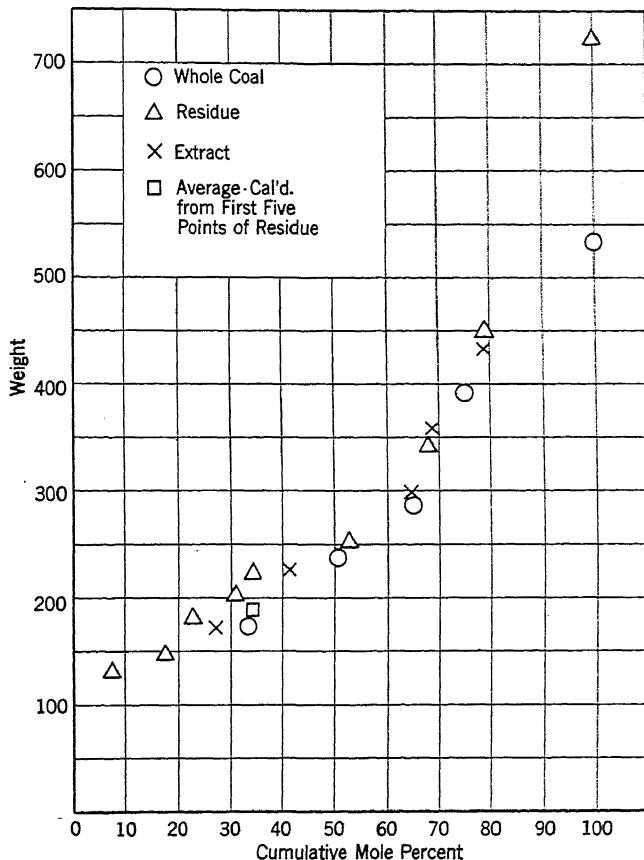


Fig. 3. Molecular weights of various fractions of cyclohexane soluble oils obtained in the hydrogenation of whole coal and the extract and residue from the benzene extraction of the coal.²⁶

formate, sought to establish whether any particular constituent of coal was especially susceptible to liquefaction. They found that humic acids extracted from a brown coal by aqueous ammonia gave on reduction the same yields of ether-soluble oils, gases, and insoluble residue as did a bitumen-rich (humic-acid-poor) coal and a

brown coal and lignites has been studied by Veisel'berg.⁴⁸ The bitumen was separated by extraction in a Soxhlet apparatus with an alcohol-benzene mixture (1:1); the humic acids were separated from the residue of the bitumen extraction by dis-

⁴⁸ Veisel'berg, K. B., *Khim. Tverdogo Topliva*, **8**, 232-46 (1937).

solving with warm 5 percent sodium carbonate solution and reprecipitating the humic acids with 10 percent aqueous hydrochloric acid. From the brown coal were separated 17.5 percent bitumen and 64.7 percent humic acids; from the lignite were separated 30 percent bitumen and 60 percent humic acid. Upon hydrogenation at 450° C for 1 hour in the presence of molybdenum sulfide catalyst the bitumens yielded 70 percent of oil containing paraffin and cyclic hydrocarbons with only small amounts of phenols; humic acids yielded 45 percent of oil containing cyclic hydrocarbons and considerable phenols. Humic acids from peat hydrogenated at 410° C for 2 hours in the presence of molybdenum sulfide catalyst yielded ⁴⁹ 34 percent of liquid products composed of aromatic and hydroaromatic hydrocarbons and of phenols.

A report ⁵⁰ on the hydrogenation of oxidized coal supports this evidence that the bitumens and humic acids of coal have a similar nuclear structure and that their different chemical behavior is the result of differences in peripheral groups. A coal which gave a 40.9 percent residue on hydrogenation was oxidized by heating in air at 150° C until an oxygen content of 27 percent was reached and the coal was 96 percent soluble in alkali. This oxidized coal upon hydrogenation still showed 37.6 percent residue and no change in the composition of the liquefied product, indicating that the oxidation of the coal substance to produce alkali-soluble "humic acids" had not degraded the coal substance (or formed a new substance capable of being degraded by hydrogenation) to such an extent that

any difference in the nature of the hydrogenation products could be detected.

The available data thus indicate that the hydrogenation products from the whole coal represent about equally well the products from any single chemical component and suggest that their general skeletal structures are similar and that such differences as do exist are due either to peripheral groups (carboxyl and hydroxyl groups to confer alkali solubility on the humic acids) or to various degrees of polymerization (to account for the differences in solubility in benzene of parts of the coal).

Concerning the constituents that are not resolved into soluble products, that is, parts of the fusain and opaque attritus, and the anthracite coals, it can only be speculated that a polynuclear cyclic structure of a far greater degree of condensation would account for their inert characteristics.

RELATION BETWEEN RANK OF COAL AND NATURE OF THE REDUCTION PRODUCTS

The patent disclosures of Bergius ² which pointed out that only coals containing less than 85 percent carbon are suitable for conversion into oils suggest that the nature of the products might vary with the rank of the coal. Fischer and Tropsch ³ showed that the hydriodic acid reduction of coal proceeded more readily with younger coals. Four bituminous coals having coke yields of 89, 85, 78, and 64 percent gave under identical conditions of reduction 12.1, 17.7, 54.6, and 70.3 percent of chloroform-soluble products, respectively. A cannel coal and a brown coal gave 49 and 60 percent respectively of chloroform-soluble products. The authors stated that the products from the various coal had essentially the same properties.

Fischer and Schrader ⁴ obtained material balances for the ether-soluble fraction, the

⁴⁹ Orlov, N. A., Tishchenko, V. V., and Tarasenkova, E. M., *J. Applied Chem. (U.S.S.R.)*, **8**, 501-4 (1935).

⁵⁰ *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March 31, 1936*, p. 152.

insoluble fraction, and the gases resulting from the reduction of coals of various ranks by means of aqueous sodium formate at 400° C. They showed that there was an increased conversion to low-molecular-weight material with decrease in rank of the coal (Table XIX).

TABLE XIX

PRODUCTS OF THE REDUCTION OF COALS OF VARIOUS RANK BY AQUEOUS SODIUM FORMATE AT 400° C⁴

Coal	Percent of Dry, Ash-Free Coal		
	Ether Soluble	Residue	Gas
Anthracite	1.6	95.5	2.9
Lean coal	10.7	74.7	14.6
Fat coal	9.2	68.7	22.1
Flame coal	39.2	46.9	13.9
Cannel coal	28.2	22.3	49.5
Brown coal	45.0	6.6	48.4
Lignite	26.8	10.2	63.0
Peat	24.2	4.7	71.1
Lignin	22.3	35.4	42.3
Cellulose	12.9	3.2	83.9

Graham and Skinner³² summarized a series of investigations^{30, 51} in which it was shown that the hydrogenation of English coals of various ranks using phenol as a vehicle resulted in phenol-insoluble residues ranging from 20 percent for lignites to 90 percent for anthracite coals. Some similar⁵² work on American coals was inconclusive, possibly because of lack of agitation of the reaction mixture.

Boomer, Saddington, and Edwards⁵³ have published a materials balance of the products of the hydrogenation of thirteen Canadian coals ranging in rank from an-

thracite to lignite. The hydrogenations were carried out in a batch autoclave at 450° C with tetralin as a vehicle and molybdc oxide as catalyst. These material balances, Table XX and Fig. 4, show that for a given hydrogenation treatment the yield of lower-molecular-weight material increases with decrease in rank of the coal treated.

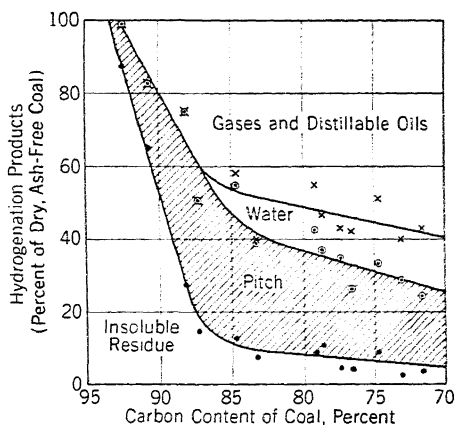


FIG. 4. Effect of rank of coal on the nature of the hydrogenation products.⁵³

The work of LeClaire,²⁷ discussed previously, showed that for four bituminous coals of different ultimate carbon content the petroleum-ether-soluble portions of the hydrogenation products were quite similar except that the products from the coals of lower carbon content were, on an average, of slightly lower molecular weight.

The hydrogenation-liquefaction of petrographic constituents from coals of various ranks^{40, 41, 42, 43} was discussed along with other work on these constituents. Conditions were such that only the more unreactive constituents, fusain and opaque attritus, showed increased liquefaction with decrease in rank. There was a not well-established trend of the heavy fractions of the liquefied products to contain more oxy-

⁵¹ Shatwell, H. G., and Bowen, A. R., *Fuel*, **4**, 252-5 (1925). Skinner, D. G., and Graham, J. I., *ibid.*, **4**, 474-85 (1925).

⁵² Beuschlein, W. L., and Wright, C. C., *Ind. Eng. Chem.*, **24**, 1010-2 (1932), **26**, 465-6 (1934).

⁵³ Boomer, E. H., Saddington, A. W., and Edwards, J., *Can. J. Research*, **13B**, 11-27 (1935).

TABLE XX

MATERIALS BALANCE OF PRODUCTS FROM THE HYDROGENATION OF
THIRTEEN CANADIAN COALS⁵⁵

		A	B	C	D	E	F	G	H	J	K	L	M	N
Ultimate analysis of the	C	92.45	90.65	88.30	87.25	84.70	83.30	79.10	78.65	77.40	76.70	74.9	73.10	71.65
dry, ash-free coals:	H	4.05	4.40	5.20	5.60	5.55	6.05	5.4	5.30	5.2	5.15	5.25	5.2	5.15
	O	1.6	2.5	4.8	5.2	8.1	7.8	13.1	14.4	14.8	15.4	17.8	20.1	21.7
	C/H	23.1	20.8	17.1	15.6	15.3	13.9	14.8	14.8	15.0	15.0	14.4	14.2	13.9
Hydrogenation products:														
Organic residue		87.8	65.1	27.7	15.0	13.0	8.0	9.3	10.7	4.9	4.3	8.8	3.3	3.8
Pitch, b.p. > 300° C		11.5	28.3	47.0	37.8	42.4	30.6	32.8	26.4	29.4	21.8	24.5	25.3	20.3
Gases and distillable oils		0.7	6.6	24.7	47.2	41.9	60.1	44.9	52.9	57.2	57.7	48.9	59.9	57.5
Water		0.0	0.0	0.6	0.0	2.7	1.3	13.0	10.0	8.5	16.2	17.8	11.5	18.4

gen as the rank of the parent substance decreased. However, the light or distillate fractions showed a well-defined increase in phenol content with decrease in rank of the parent substance. The gaseous products from the lower-rank material also showed a greater carbon dioxide content. Warren and Bowles¹⁵ also noted that the oxygen of lower-rank coals, although appearing largely as carbon dioxide and water in the hydrogenation products, appeared also in the form of increased phenolic content of the oils as the oxygen content of the coals increased. This effect of rank on the reduction products of coal suggests that younger coals are characterized by a structure in which the points of fission are more numerous and peripheral groups containing oxygen are more abundant, but in which the stable or fission-resisting units are of the same nature, except for a smaller size, as those in more mature coals.

Since, as commonly accepted, coal has been formed from the accumulated remains of plant life which have undergone a series of reactions termed "coalification," it is of interest to note the results of the reduction or hydrogenolysis of the plant remains before coalification has set in. Willstätter and Kalb⁵⁴ reduced lignin by means of hydriodic acid and phosphorus in sealed

tubes at 280° C to obtain a mixture of hydrocarbons boiling from 200° C at atmospheric pressure to 250° C at 2 millimeters with molecular weights from 170 to 350 and atomic hydrogen-to-carbon ratios of 1.82 to 1.64. A nondistilling residue had a molecular weight of 725-850 and a hydrogen-to-carbon ratio of 1.63 to 1.58. The authors pointed out that the hydrocarbons must be a mixture of polycyclic hydrogenated ring structures, and later Schrauth⁵⁵ showed that the largest fraction was identical in physical and optical properties with his synthetic preparation of perhydrotriphenylene. The hydrogenation⁵⁶ of lignin from aspen wood at 250° C over copper chromite catalyst yielded methyl alcohol and oxygenated derivatives of alkyl cyclohexanes and 35 percent of high-boiling products which from their analysis and boiling point had an average composition of $C_{15}H_{32}O_3$ or $C_{24}H_{24}O_4$.

The hydrogenation of wood⁵⁷ in a tetralin medium without catalyst yielded water (strongly acidic), light aldehydic smelling oils, and small amounts of pitch, but no residue.

⁵⁵ Schrauth, W., *Z. angew. Chem.*, **36**, 149-52, 571 (1923).

⁵⁶ Harris, E. E., D'Ianni, J., and Adkins, H., *J. Am. Chem. Soc.*, **60**, 1467-70 (1938).

⁵⁷ Boomer, E. H., Argue, G. H., and Edwards, J., *Can. J. Research*, **13B**, 337-42 (1935).

⁵⁴ Willstätter, R., and Kalb, L., *Ber.*, **55**, 2637-52 (1922).

Cellulose treated⁵⁸ at 440° C with hydrogen at 120 atmospheres in the presence of nickel oxide was completely converted to soluble and gaseous products: the 22.4 percent of soluble products consisted of 77 percent neutral oil, 2.3 percent phenols, and 22.4 percent of a brown powder insoluble in ether.

Bergius⁵⁹ subjected cellulose to thermal decomposition in a closed vessel under pressure of the autogeneous gases to obtain a coallike substance which on hydrogenation gave small quantities of oil resembling petroleum.

These meager data on hydrogenation of plant-life remains indicate that these remains must have undergone considerable alteration during coalification in order to attain the resistance to degradation by hydrogenolysis that is exhibited by coal.

MECHANISM OF THE FORMATION OF THE HYDROGENATION PRODUCTS AND THEIR PRIMARY NATURE

It was recognized rather early that the production of low-molecular-weight substances by the action of reducing agents on coal was a combination of thermal cracking and hydrogenation. Kling⁶⁰ considered the process of Bergius to be one of dissociation similar to the reaction $2HI \rightleftharpoons H_2 + I_2$ except that the dissociation products of hydrocarbons were unstable and the reaction was not reversible. Bergius⁶¹ described his process of liquefaction as a competition between hydrogenation and destructive distillation. Hlavica⁶² distin-

guished two phases of the reaction, the initial phase characterized by large hydrogen absorption and little formation of gases and yielding an asphaltic product, and a second phase in which hydrogen absorption is small and gas formation large, and the product becomes a low-molecular-weight oil. The initial phase may be regarded as a combination of depolymerization with subsequent hydrogenation; the second phase involves cracking and some hydrogenation of the fragments.

The primary liquefaction of coal by hydrogenation is characterized, especially in the early stages, by the elimination of oxygen, principally as water, but also as carbon dioxide and low-molecular-weight phenols.⁶³ This oxygen which is easily eliminated is probably combined differently from the remainder of the oxygen. Where the reaction has been exhaustive, nearly all the oxygen may, of course, appear as water or carbon dioxide.⁶³

The effect of physical variables upon the physical and chemical composition of the products from the continuous hydrogenation of coal gives some information of the mechanism of the process. In Table XXI are given some data on the distribution of oxygen among the hydrogenation products of a bituminous coal at various degrees of conversion to volatile products. The hydrogenations were carried out in a continuous plant, and the extent of reaction is expressed in the ratio of overhead (volatile) to heavy (nonvolatile) oils.

Table XXI shows that 45 percent of the oxygen appears as water and carbon dioxide when the ratio of overhead to heavy oil is small, and the heavy oils account for twice the oxygen accounted for in the overhead oils. At higher ratios of overhead to heavy oil, the oxygen in the

⁵⁸ Bowen, A. R., Shatwell, H. G., and Nash, A. W., *J. Soc. Chem. Ind.*, **44**, 507-11T, 526T (1925).

⁵⁹ Bergius, F., *J. Soc. Chem. Ind.*, **32**, 462-7 (1913).

⁶⁰ Kling, A. J., *Chimie & industrie*, **11**, 1067-77 (1924).

⁶¹ Bergius, F., *Ind. Eng. Chem., News Ed.*, **4**, No. 23, 9-10 (1926).

⁶² Hlavica, B., *Brennstoff-Chem.*, **9**, 229-31 (1928).

⁶³ Von Makray, I., *Brennstoff-Chem.*, **11**, 61-4 (1930).

TABLE XXI

OXYGEN DISTRIBUTION IN HYDROGENATION
PRODUCTS¹⁰

H ₂ O	Total Oxygen in		Ratio of	
	CO ₂	Overhead Oil	Heavy Oil	Oil to Heavy Oil
percent	percent	percent	percent	
42.4	3.0	18.2	36.4	0.41
45.2	2.3	22.6	29.9	0.62
50.0	6.2	20.8	23.0	0.78
47.4	2.8	28.6	21.2	0.90
51.9	6.2	28.1	13.8	1.38
58.3	6.6	23.1	12.0	1.68
59.4	5.9	29.7	5.0	1.72

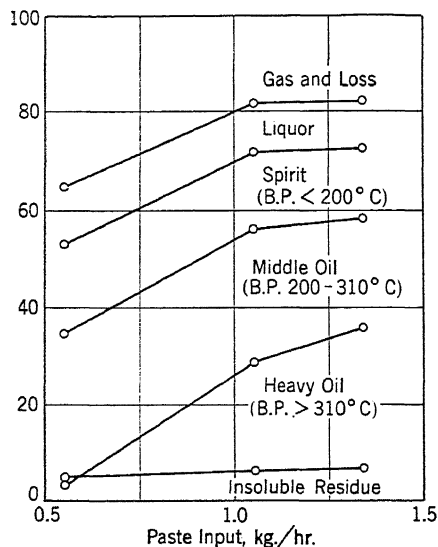
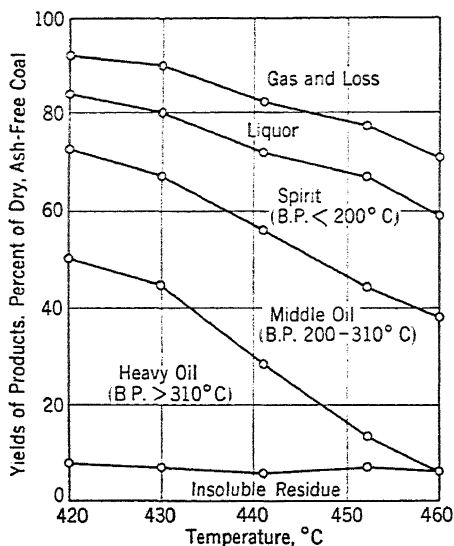
heavy oils diminishes and that in the overhead oil increases, but not proportionately, increased formation of water and carbon dioxide accounting for the difference. Although the oxygen in the heavy oils may pass directly to water, the increase in oxygen content of the overhead oils with increased conversion and the fact that oxygen in the overhead oils is almost exclusively phenolic at both low and high con-

versions favors the overhead oils as an intermediate step, the mechanism being:

Heavy oil oxygen → Overhead oil phenols
→ Hydrocarbons plus water

Booth and Williams⁶⁴ varied hydrogen input, hydrogen pressure, paste input (reaction time), and temperature from standard conditions of 1,600 liters per hour of hydrogen, 1 kilogram per hour of paste (4 hours' reaction time), 200 atmospheres pressure, and a temperature of 440° C. Hydrogen input and pressure had little effect, but Figs. 5 and 6 show the different yields of various products as temperature and time of reaction were varied. It is apparent that the formation of soluble products is the first step in the degradation, being 90 to 95 percent complete under the mildest conditions reported. The reactions which produce increasing amounts

⁶⁴ Booth, N., and Williams, F. A., *J. Inst. Fuel*, **11**, 493-502 (1938).



FIGS. 5 and 6. Effect of temperature and time (paste input) on yields of various products from hydrogenation of coal in a continuous plant.⁶⁴

of low-boiling material require higher temperatures and longer reaction time. The nearly parallel lines for yields of materials of various boiling ranges indicate that the reactions involved have approximately the same energy requirement, which is considerably greater than the energy requirement for the reaction giving rise to soluble products. The uniformity of energy requirements for the steps heavy oil to middle oil to spirit to gas, and the fact that the last step is undoubtedly a cracking reaction, indicate that all these steps are the result of cracking reactions. The formation of soluble products has proceeded so far under the mildest conditions recorded in this research that no conclusions can be drawn as to relative energy requirements of this reaction. However, inasmuch as this first step takes place so much more readily than the succeeding steps, the degradation probably involves the breaking of weaker bonds than those involved in the degradation of heavy oil to light oil. A degradation reaction such as depolymerization is indicated.

Since the conversion to lighter products appears to be a stepwise process: Residue \rightarrow Heavy oil \rightarrow Middle oil \rightarrow Light oil \rightarrow Gas (some gas formation, of course, accompanies each step), and the essential cyclic nature of the middle oils appears to be the same whether a small or large fraction of heavy oil has been converted to lighter material, conclusions as to the carbon-to-carbon bonding in coal drawn from the nature of the middle oils are applicable to a large percentage of the carbon appearing as heavy oil. Carbon in insoluble residues, especially where drastic treatment has been resorted to, probably should not fall in the category of the carbon in the heavy oils. Although the general nature of the carbon and oxygen linkages of the heavy oils may be inferred from those of the middle oils

regardless of the extent of the reaction, the relative distribution of sizes of stable nuclei is safely arrived at only when no extensive cracking or rupture of carbon-to-carbon bonds has taken place, that is, only when conditions have been such that large amounts of gaseous hydrocarbons have not been formed. It is significant that, even with bituminous coals, 60 to 70 percent of the carbon of the coal can be converted to soluble products of which 40 percent or more are distillable products without appreciable formation of hydrocarbon gases.^{26, 27}

Horton, King, and Williams⁶⁵ used a hydrogen recirculating system with appropriate traps to determine the change with time in composition of the volatile oils from the hydrogenation of coal. From Table XXII it is evident that the phenols are formed largely in the earlier part of the reaction. It is probable that the phenols formed later in the reaction at this temperature are destroyed as fast as formed. Additional results at a lower reaction temperature would be very instructive.

The results of some unpublished experimental work done in Germany were reported³⁸ as indicating that primary hydrogenation of coal is a stoichiometric reaction at 360° C. In the hydrogenation products, 20 percent of the carbon always appeared as gases and 80 percent as solid or liquid products. Half of the oxygen remained in the solid or liquid products which have a composition expressed by the formula $(C_{16}H_{16}O)_x$. Fractionation of this hydrogenation product gave a series of substances all having a carbon-to-oxygen ratio of 16, but with a hydrogen content of 12 to 24 atoms per 16 carbon atoms. Coal was regarded as built up of uniform building

⁶⁵ Horton, L., King, J. G., and Williams, F. A., *J. Inst. Fuel*, **7**, 85-102 (1933).

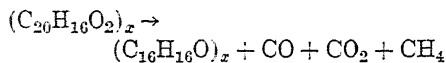
TABLE XXII

COMPOSITION OF OILS PRODUCED AT DIFFERENT STAGES IN THE HYDROGENATION OF COAL, PERCENTAGE OF ASH-FREE COAL ⁶⁵

Charge	Components	Up to Reaction Tem- perature*	During Interval at Reaction Temperature			
			1st Hour	2nd Hour	3rd Hour	Total
		percent	percent	percent	percent	percent
Coal alone	Phenols	4.5	0.8		0.1	5.4
	Bases	0.8	0.4		0.2	1.4
	Neutral oil	13.2	4.4		6.4	24.0
	Pitch	3.1	1.8		2.5	7.4
	Total	21.6	7.4		9.2	38.2
Coal + 0.1% SnOH	Phenols	2.7	1.2	0.2	0.1	4.2
	Bases	0.5	0.8	0.4	0.4	2.1
	Neutral oil	14.5	14.0	9.0	13.8	51.3
	Pitch	1.6
	Total	17.7	16.0	9.6	15.9	57.6
Coal + Vehicle	Phenols	3.9	1.6	5.5
	Bases	0.8	0.5	...	0.3	1.6
	Neutral oil	10.8	13.8	3.6	11.6	39.8
	Pitch	-0.1	1.9	1.8
	Total	15.5	15.9	3.5	13.8	48.7
Coal + Vehicle and 0.1% SnOH	Phenols	4.3	1.5	0.3	0.3	6.4
	Bases	1.5	0.6	0.1	0.6	2.8
	Neutral oil	18.3	16.1	5.9	12.5	52.8
	Pitch	<.01	1.0	1.6	2.5
	Total	24.1	18.1	7.3	15.0	64.5

* Four hours to 400° C; 1 hour, 400 to 450° C; reaction temperature, 450° C.

units, and the hydrogenation reaction was written:



Some data on the kinetics of the primary liquefaction of coal by hydrogenation have been published by Storch and his coworkers at the U. S. Bureau of Mines.^{55, 56, 57}

⁵⁶ Storch, H. H., Fisher, C. H., Eisner, A., and Clark, L., *Ind. Eng. Chem.*, **32**, 346-53 (1940).

This work was done in a rotating 1.2-liter bomb, using equal weights (100 grams each) of tetralin and coal plus 1 percent of tin sulfide. The relationship between liquefaction and hydrogen consumption and oxygen removal and the effect of time and temperature were studied. The extent of liquefaction was measured in terms of solu-

⁵⁷ Fisher, C. H., Sprunk, G. C., Eisner, A., Clark, L., Fein, M. L., and Storch, H. H., *Fuel*, **19**, 132-8 (1940).

bility in acetone and benzene. Oxygen removed was arbitrarily defined as the oxygen not remaining in the acetone-insoluble residue or the pitch left after distilling from the soluble material everything volatile up to 215° C. A Pittsburgh Seam coal from the U. S. Bureau of Mines' experimental mine at Bruceton, Pa., was studied

whose slopes show a temperature coefficient of about 1.2 for a 10° C temperature change. This rather low temperature coefficient indicates that the slow step involved is probably a diffusion process. The hydrogen molecule is probably not involved in this rate fixing because its speed of diffusion as the result of its small size

TABLE XXIII⁶⁷
ANALYSES OF ANTHRAXYLONS (PERCENTAGE BY WEIGHT)

		Ultimate (Dry, Ash-Free Basis)						
No.	State or Country	Hydro- gen	Car- bon	Nitro- gen	Oxy- gen	Sul- fur	C H	Calorific Value
		percent	percent	percent	percent	percent	C H *	calories per gram
1	Washington	4.9	74.6	0.3	19.9	0.3	15.2	31.7
2	Washington	4.0	74.2	0.4	20.1	0.3	14.8	30.9
3	Denmark (Faroe Islands)	5.0	76.5	0.6	17.5	0.4	15.3	28.3
4	Denmark (Faroe Islands)	4.7	75.6	0.5	18.8	0.4	16.1	33.6
5	Ohio	5.6	81.5	1.6	8.3	3.0	14.6	19.2
6	Ohio	5.5	81.7	1.6	8.3	2.9	14.9	19.7
7	Pennsylvania †	5.5	84.5	1.6	7.3	1.1	15.4	19.8
8	Pennsylvania ‡	5.3	87.1	1.7	5.0	0.9	16.4	20.1

* Carbon/available hydrogen; available hydrogen = $\% \text{H} - \frac{\% \text{O}}{8} - \frac{\% \text{N}}{5}$.

† Pittsburgh, Allegheny County.

‡ Westmoreland County.

initially, and then, in order to evaluate the effect of rank and eliminate effects that might result from differences in petrographic composition, anthraxylon separated from several coals of different ranks was studied. The five anthraxylon samples selected contained from 5 to 20 percent oxygen; their ultimate composition is shown in Table XXIII.

Rate of Hydrogen Consumption.^{66, 67}

Figure 7 shows the rate at which hydrogen was consumed at various temperatures. After a steep rise during the first hour the curves of hydrogen consumption *versus* time are a series of virtually straight lines

is much greater than that of the other molecules involved. Changes in rate of hydrogenation resulting from change in hydrogen pressure are probably due both to changes in the amount of hydrogen adsorbed on the catalyst and to displacements of the equilibria involved. The change in slope of the 415° C curve at about 9 hours may be due to reversible hydrogenation of unsaturated compounds, the equilibrium favoring saturation at 400° C changing rapidly at higher temperatures in favor of the unsaturated molecules. This statement is also supported by Fig. 8, which shows that the maximum hydrogen content of the

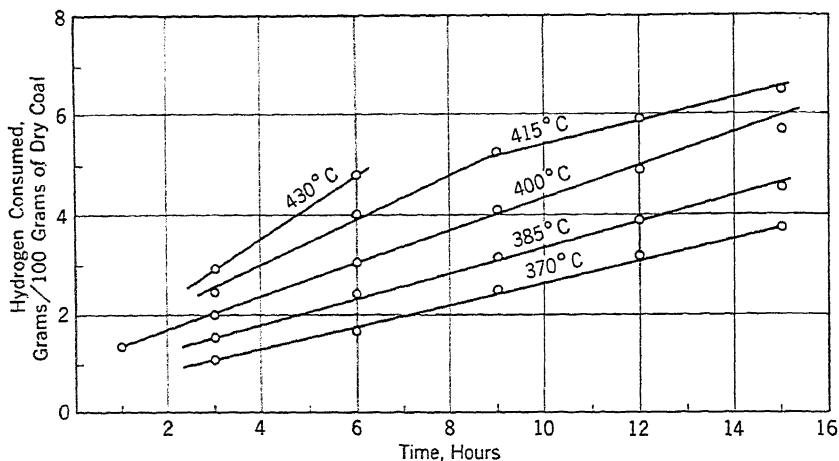


FIG. 7. Rate of hydrogen consumption during hydrogenation of coal.^{66, 67}

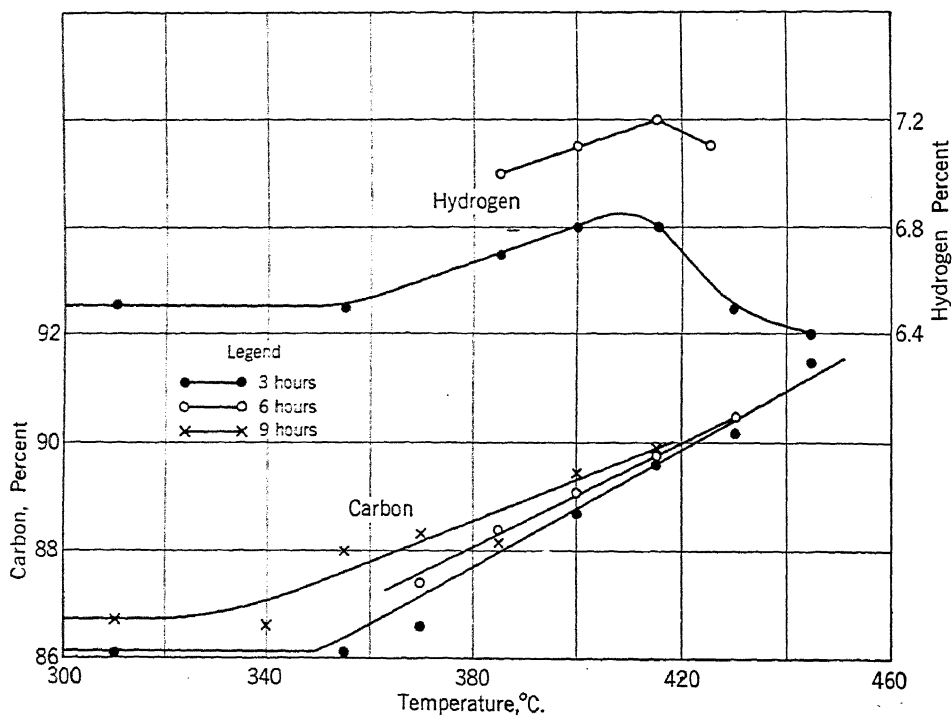


FIG. 8. Effect of temperature of hydrogenation of coal on carbon and hydrogen contents of resulting pitches.^{66, 67}

main product (pitch) occurs at about 410°C . The steep rise of the curve for hydrogen consumption during the first hour may be due to a combination of reaction at the surface layer of the coal particles and diffusion of hydrogen into the body of the coal particle as it becomes

from Fig. 15 that beyond 80 percent liquefaction hydrogen consumption continues with only little change in the degree of liquefaction, which indicates that the principal reaction in this region is that of hydrogen with the liquid phase. Figure 11, where hydrogen consumption is plotted

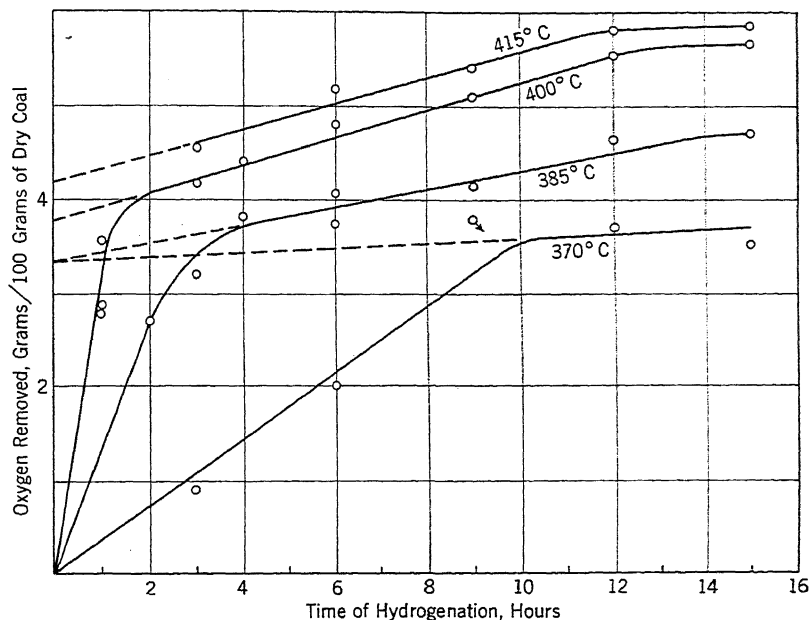


FIG. 9. Rate of oxygen removal from coal during hydrogenation.^{66, 67}

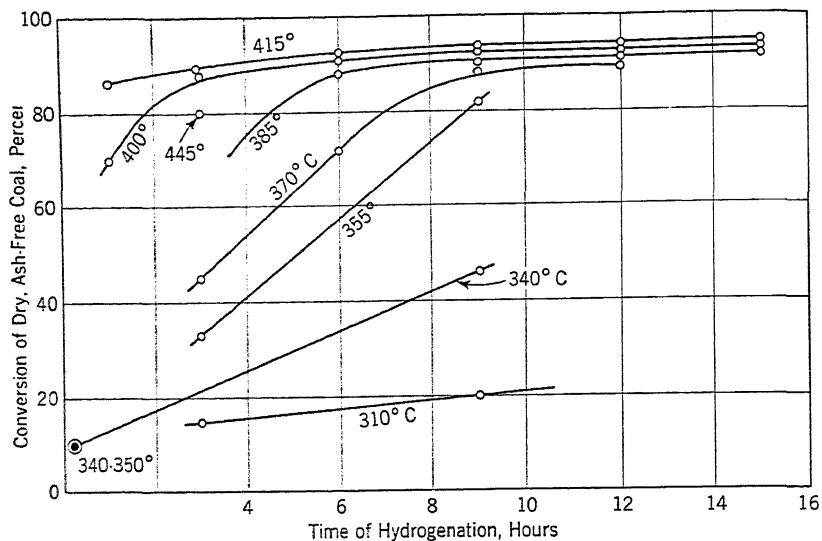
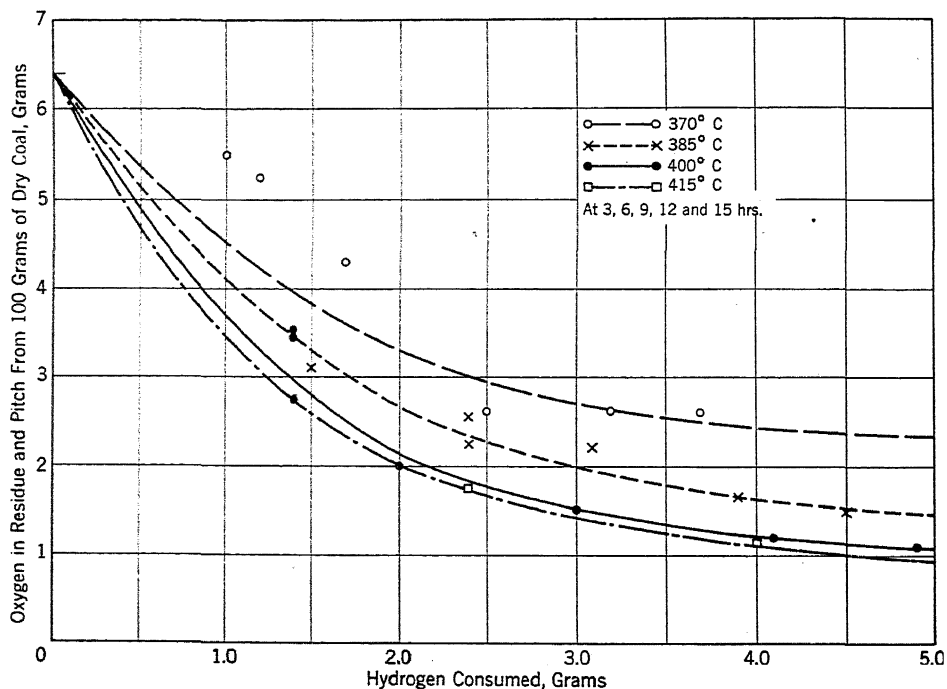
more permeable as the result of solvent action and heat.

The curves of Fig. 7 are characteristically different from those for the rates of oxygen elimination and of coal liquefaction as given in Figs. 9 and 10, respectively. These comparisons show that there is no direct or simple relation between the hydrogen consumption and either oxygen removal or liquefaction. Such a relation was scarcely to be expected in view of the considerable number of possible hydrogen-consuming reactions that may have been taking place concurrently. It is evident

against oxygen elimination, shows that hydrogen consumption continues long after the majority of the oxygen has been eliminated.

As to the effect of the rank of a coal upon hydrogen consumption, Fig. 12 shows that, of five anthraxylons of different rank, the anthraxylon of lowest rank and highest oxygen content (Washington) consumed the least hydrogen and had the lowest rate of hydrogen consumption. However, no definite trend is noted; Ohio anthraxylon, which was of intermediate rank and oxygen content, showed the highest

CHEMICAL CONSTITUTION OF COAL

FIG. 10. Effect of time on liquefaction yield.^{66, 67}FIG. 11. Relation between oxygen remaining in coal and the amount of hydrogen consumed during the hydrogenation of coal.^{66, 67}

hydrogen consumption. Data on a larger number of samples are required, and a careful evaluation of possible factors such as resin content should be made. The constant rate of hydrogen consumption after the first hour characterizes all the anthraxylons as it did the whole coal.

Rate of Liquefaction.^{66, 67} Inasmuch as liquefaction was measured by determining the amount of material remaining insoluble

using the equation for a first-order reaction is given in Fig. 13. When corrected for the rate of heating to reaction temperature the initial slopes (at $t = 30$ minutes) yield the following temperature coefficients:

Temperature interval, °C	310-355	355-370	370-385	385-400
Temperature coefficient per 15° C	1.5	1.8		
Activation energy, kilogram calories	6.6	32.0	56.0	65.0

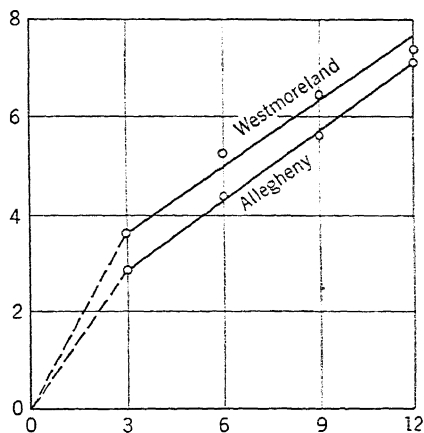
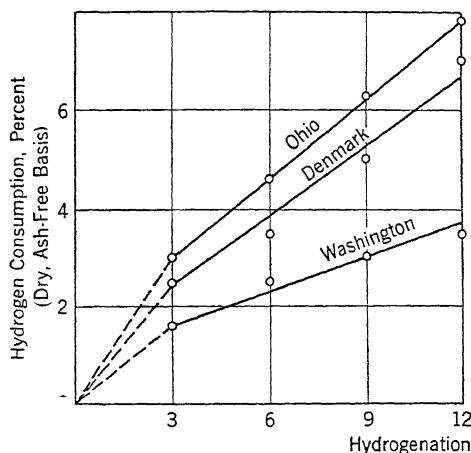


FIG. 12. Rate of hydrogen consumption for various anthraxylon samples.^{66, 67}

in acetone and benzene, it is apparent that "liquefaction" means decrease in molecular weight until the products are gaseous under normal conditions or are dissolved by the solvent treatment. Any further decrease in molecular weight is not evaluated by the percentage liquefaction.

Figure 10 shows the percentage conversion into soluble material plus gases at various times and temperatures. Since the extent of liquefaction is independent of the rate of consumption of hydrogen and virtually all the vehicle was recovered as such, the rate of liquefaction may be considered to depend only upon the concentration of the coal substance. A plot of the data

At 8 and 12 hours the temperature coefficients are as follows:

Temperature interval, °C	310-355	355-370	370-385	385-400
Temperature coefficient per 15° C				
$t = 8$ hours	1.5	1.2	-3.0	-1.1
$t = 12$ hours	...		-3.4	-1.4
Activation energy, kilogram calories	6.6	10.0	?	?

The temperature coefficients (at $t = 30$ minutes) indicate that at least two processes are involved in the liquefaction process: (1) One is solution or extraction of the coal substance, characterized by a low temperature coefficient of about 1.2 per 10° C and by the fact that it appears to be

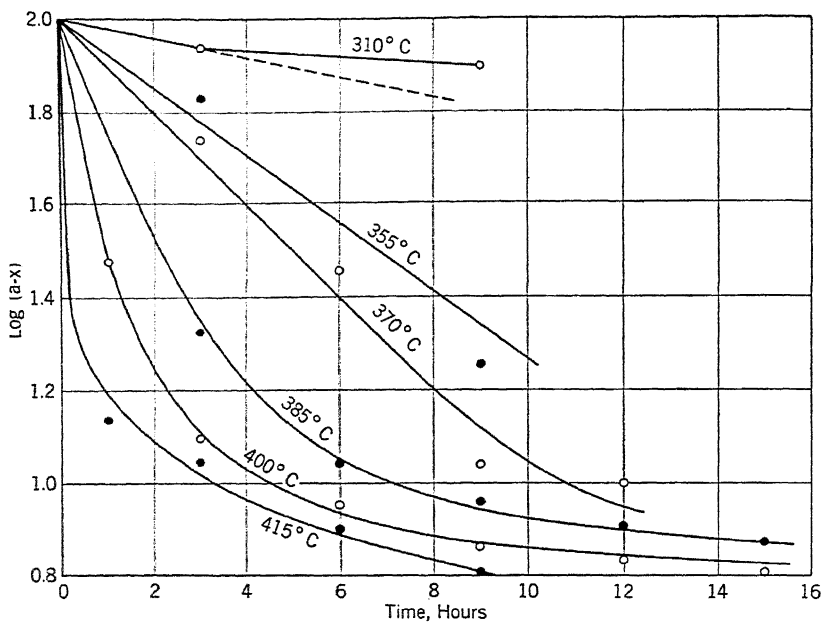


FIG. 13. Liquefaction data presented as first-order reactions.^{66, 67}

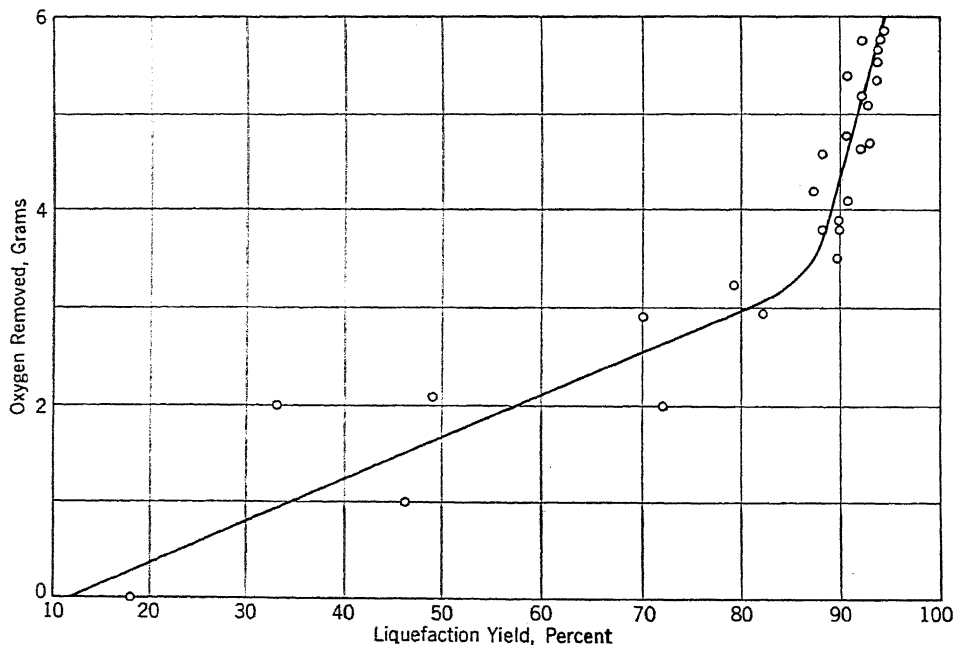


FIG. 14. Relation between oxygen removed and conversion of dry, ash-free coal into gases and benzene-soluble materials, presenting data for all temperatures and times of reaction studied.^{66, 67}

the principal process occurring at temperatures below 370° C. The limiting factor in this process is probably diffusion of the dissolved material away from the solute surface. (2) Beyond 370° C the temperature coefficient of liquefaction increases rapidly to about 2.0 per 10° C, the activa-

The apparent negative temperature coefficients at $t = 8$ and 12 hours for temperatures above 370° C may be caused by the fact that the coal substance is not a chemically pure material and that its constituents (anthraxylon, translucent attritus, and opaque attritus) have different first-

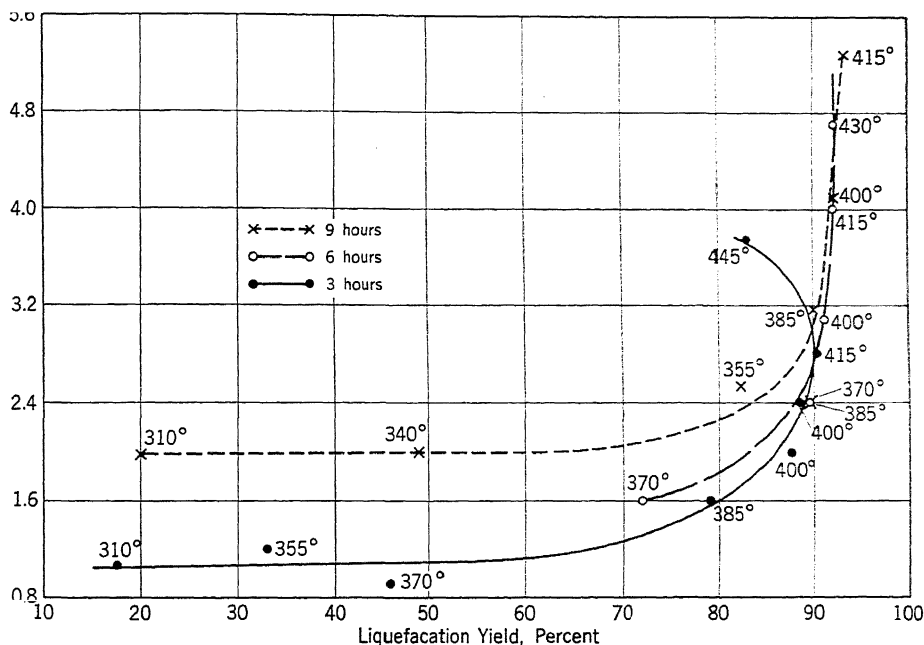


Fig. 15. Liquefaction yields and hydrogen consumption.^{66, 67}

tion energy remaining at about 60 kilocalories in the range 370 to 415° C, indicating that a chemical reaction, probably a thermal decomposition of the coal substance, is effecting liquefaction. This thermal decomposition may or may not be identical with the reaction causing the rapid elimination of 60 percent of the oxygen. (See Fig. 14.) Immediately after the production of free radicals or unsaturated molecules by the thermal decomposition reaction, most of these units are stabilized by catalytic hydrogenation.

order rate constants. An additional possibility in explaining these negative temperature coefficients is the precipitation of polymers formed by condensation of the products of the initial thermal decomposition before the products could be stabilized by reaction with hydrogen. These polymers are more stable than the original coal substance, and hence the rate constants for their liquefaction would be smaller than for the original coal. At temperatures of about 440° C and pressure of 180 atmospheres of hydrogen the rate of precipita-

tion of polymers exceeds the rate of liquefaction; hence, increased amounts of residue appear which are commonly designated as coke. This is well shown in Fig. 15, where liquefaction yield is plotted against hydro-

two anthraxylons of lowest rank, and, as for hydrogen consumption, the implied correlation between rank and liquefaction rate should be verified by further experiments. With data at only one temperature for the

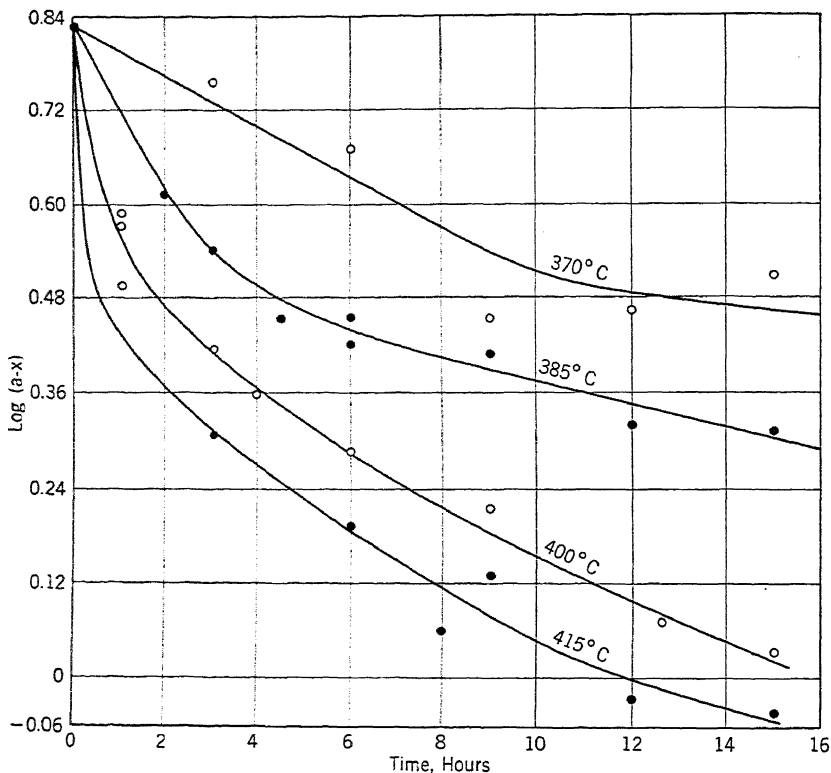


FIG. 16. Oxygen removal during the hydrogenation of coal, plotted as first-order reactions.^{66, 67}

gen consumption; the reversion, just above 400° C, of the curve for liquefaction yields at 3 hours is quite apparent.

The hydrogenations of the five anthraxylons of different ranks were carried out at 400° C only. At this temperature the liquefaction yields were greater than 96 percent at the end of the first 3-hour period for all samples except the Washington and Denmark anthraxylons, which were 72 and 93.4 percent, respectively. These are the

liquefaction of these relatively homogeneous materials, no temperature coefficients were available to clarify the cause of the negative temperature coefficient obtained for whole coal.

Rate of Oxygen Removal.^{66, 67} Data for the rates of oxygen removal from Bruceton coal by hydrogenation at various temperatures are shown in Fig. 9. In considering these rates, it should be recalled that they are independent of the rate of hydrogen

consumption. Also, as will be shown, the oxygen-removal rates have temperature coefficients considerably larger than those characteristic of diffusion processes, indicating that the rates measured are those of chemical reactions. The abrupt changes in slope of the curves in Fig. 9 suggest a series of successive unimolecular reactions.

In Fig. 16, the oxygen-removal rates are plotted as if the reaction were first order with respect to the concentration of coal substance. For a simple unimolecular reaction these curves would be straight lines. The curves of Fig. 16 indicate that the reaction is of higher order than first or consists of a number of first-order reactions of different rates.

A plot of the data according to the bimolecular equation gave completely unsatisfactory results and indicated consecutive first-order reactions for the oxygen-removal process. When corrected for a 2° C per minute rate of heating to reaction temperature, the initial slopes (to $t = 30$ minutes) of the curves of Fig. 16 yielded the following temperature coefficients:

Temperature interval, °C	370-385	385-400	400-415
Temperature coefficient per 15° C	3.4	2.9	2.8
Activation energy, kilogram calories	69	65	64

These coefficients appear to show that the initial oxygen-removal reaction above 370° is a thermal decomposition of the coal substance. At $t = 8$ and 12 hours, the temperature coefficients are:

Temperature interval, °C	370-385	385-400	400-415
Temperature coefficient per 15° C			
$t = 8$ hours	-210	2.0	-1.7
$t = 12$ hours	1.1	2.0	-1.5
Activation energy, kilogram calories	?	42	?

The negative coefficient for the interval 370-385° C up to 8 hours' reaction time may be due to the fact that the initial fast

reaction has not yet been completed at 8 hours. At 12 hours at 370-385 and at 8 hours at 385-400° C the second and slower reaction, or group of reactions, only is in evidence and a positive coefficient appears. Extrapolation to zero time of the curve for the slow rate indicates that roughly 60 percent of the oxygen of this Pittsburgh Seam coal is removed at the faster initial rate; oxygen lost as carbon dioxide is only about 6 percent of the total oxygen content. Between 400 and 415° C, the second reaction is largely obscured by some phenomenon that results in still slower oxygen removal; it may be condensation, producing more stable molecules from which oxygen is eliminated at a very slow rate. These considerations may indicate the presence of two different species of oxygen (in addition to that yielding carbon dioxide, which is only a small part of the total), or, since oxygen removal meant formation of substances volatile below 200° C, they may indicate compounds containing a single type of oxygen such as ethers which decompose thermally to yield phenolic fragments only a part of which are volatile; the removal of oxygen from the nonvolatile phenolic fragments by reduction to water and hydrocarbon then constitutes the second or slow reaction. The temperature coefficients at $t = 8$ and $t = 12$ and the activation energy of 42 kilogram calories are of doubtful accuracy, owing to overlapping of reactions with different rate constants.

More recent work by the authors cited has established that the oxygen-elimination reactions are at least in part catalytic in nature.⁶⁸

The general picture of the kinetics of oxygen removal is not altered by a difference of rank in the coal substance studied. Figure 17 shows the oxygen-removal-rate curves for the five anthraxylons of different

⁶⁸ Private communication.

ranks which were studied. Only the slow portion of the curves and their extrapolations are shown. As was true for the whole coal, roughly 60 percent of the total oxygen of the three higher-rank anthraxylons was

xylon, and the probable loss of carbon dioxide by absorption in the ammoniacal liquor also formed during hydrogenation would indicate that very likely the true figure was still higher. The presence of considerable

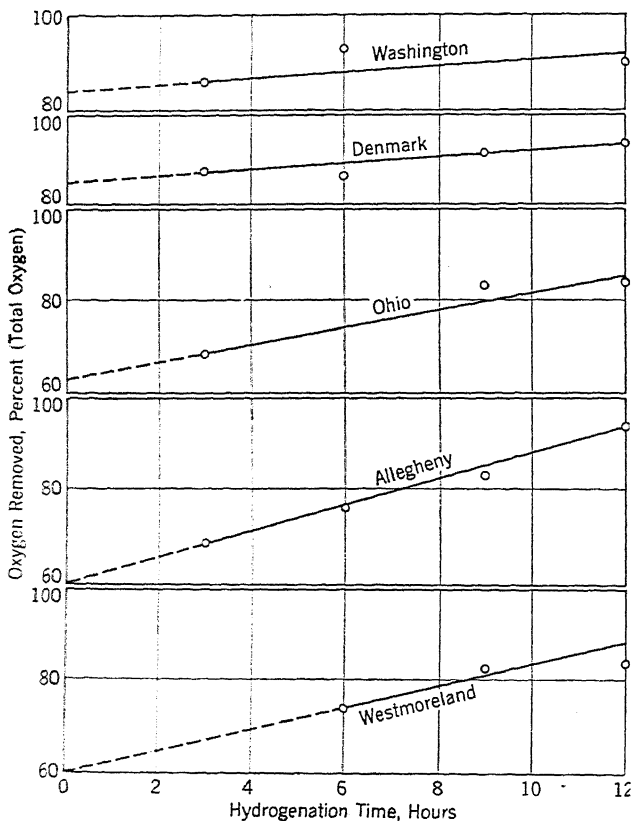


FIG. 17. Rates of oxygen removal from anthraxylons by hydrogenation at 400° C.^{66, 67}

removed by the fast reaction. For the two lower-rank anthraxylons this figure was 85 percent. The increased elimination of oxygen in the form of carbon dioxide in these two instances (see Fig. 18) accounted for a large part of the difference noted. Indeed, the oxygen actually accounted for as carbon dioxide was as high as 16.5 percent of the total oxygen in the Washington anthra-

amounts of alkali-soluble material in coals of lower rank suggests that this carbon dioxide results from the decarboxylation.

Gas Evolution.^{66, 67} The effect of temperature on the yields of gases is shown by Figs. 19 and 20. During the first 3 hours the yield of carbon dioxide increases with temperature to about 400° C and then decreases. The methane and higher hydro-

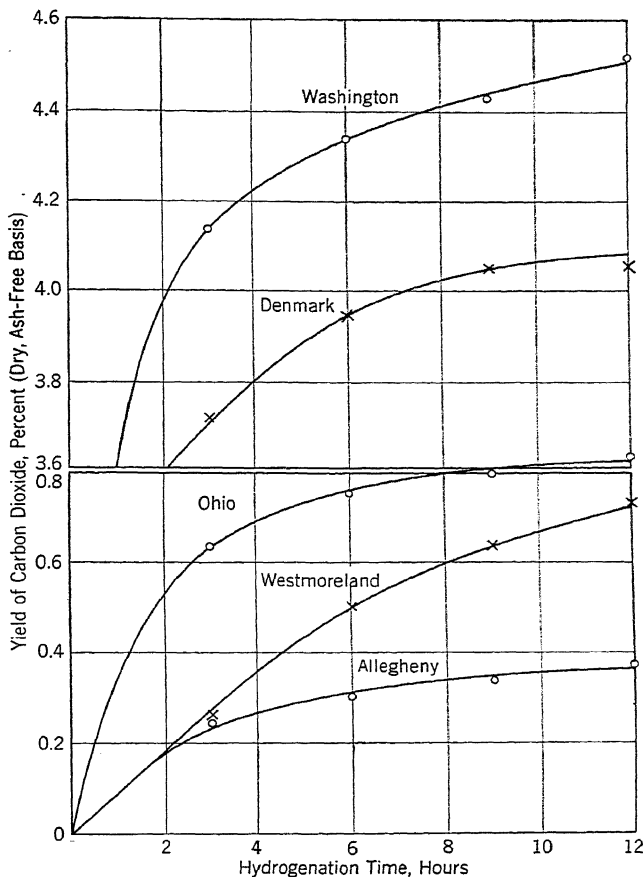


FIG. 18. Rates of carbon dioxide production from anthraxylons on hydrogenation.^{66, 67}

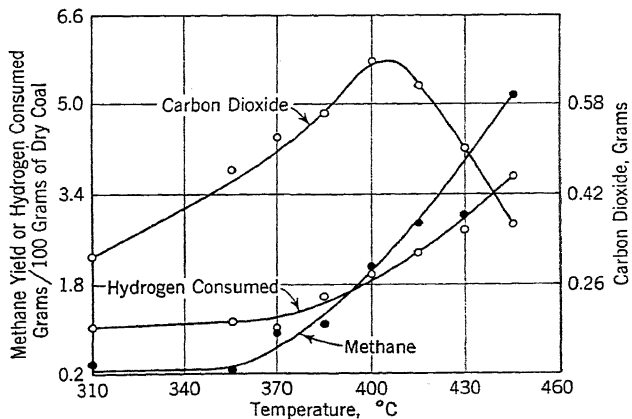


FIG. 19. Hydrogen consumption and evolution of carbon dioxide and methane during the hydrogenation of coal.^{66, 67}

carbon yields increase rapidly with temperature, especially above 400° C. Higher hydrocarbons were not found in the hydrogenation gases at temperatures of 370° C and lower, but at higher temperatures large quantities, exceeding those of methane, were indicated. Figure 19 also contains

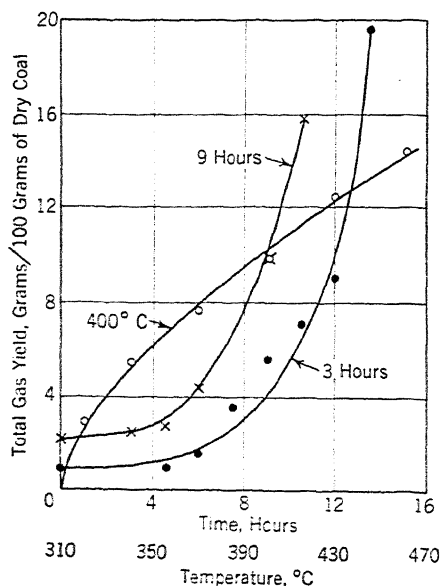


FIG. 20. Rate of gas evolution during the hydrogenation of coal.^{69, 77}

data on hydrogen consumption as a function of temperature; increasing methane production is concomitant with increasing hydrogen consumption.

Above 430° C the temperature coefficient for gas formation increases sharply with increasing temperature. It is likely that the main source of gaseous hydrocarbons above 430° C is the thermal decomposition of the products of the primary liquefaction of the coal.

Pier⁶⁹ has discussed the reactions involved in the high-pressure hydrogenation

of coal from the viewpoint of the technical production of various types of products by control of reaction conditions. Hydrogenation of coal was considered to involve three classes of reactions: (1) hydrogenation and dehydrogenation; (2) splitting, polymerization, and condensation (breaking and reforming of C—C bonds); and (3) refining (splitting off of oxygen, sulfur, and nitrogen followed by hydrogenation).

Olefinic linkages are hydrogenated at the catalyst at 200° C. Refining reactions, so called because the absence of oxygen, sulfur, and nitrogen is desirable in liquid fuels and lubricants, start as low as 300° C. At still higher temperatures, breaking of C—C bonds occurs. The initial liquefaction of the coal to a high-melting "extract" may be regarded as a depolymerization, but degradation to heavy oil and further to light oil is the result of cracking. The catalyst influences the temperature at which these reactions occur. Some catalysts cause pronounced cracking as low as 350° C. With other catalysts the refining reaction and hydrogenation may be the main reactions as high as 400° C. At 450° C, cracking is generally accompanied by hydrogenation, but it takes place at 500° C without hydrogenation and may even be accompanied by dehydrogenation. Polymerization reactions may occur simultaneously with refining and cracking reactions; they may take place more readily as the temperature is increased but may be suppressed by proper catalysts and increased hydrogen pressure. This résumé again emphasizes the necessity for low temperature, high hydrogen pressure, and careful selection of catalysts where the hydrogenation products from coal are to be the basis for a study of the chemical constitution of coal.

In addition to the information obtained from the study of the variables of the hydrogenation of coal itself, much is to be

⁶⁹ Pier, M., *Trans. Faraday Soc.*, **35**, 967-79 (1939).

learned concerning the mechanism of coal hydrogenation from a study of the destructive hydrogenation of known compounds. So far as thermodynamic considerations are concerned, all hydrocarbons except the three lowest paraffins are unstable at temperatures above 100°C and owe their continued existence above this temperature to lack of reactivity. As regards relative stability of the various hydrocarbons, the situation changes with temperature since their free energy *versus* temperature curves have different slopes. In general, the paraffins and polymethylenes (naphthenes) are relatively the more stable hydrocarbons below 225°C , whereas aromatics and olefins are more stable at higher temperatures. Aromatics with paraffinic side chains, though more stable than benzene at lower temperatures, rapidly become less stable above 450°C . Naphthalene exhibits progressively greater stability with reference to benzene above this temperature. It is quite probable that the larger condensed ring structures also exhibit the same behavior. The question of actual decomposition conditions, that is, conditions under which reactivity permits approach to thermodynamic equilibrium, remains for individual experiment. Hydrocarbons of the condensed nuclear type—naphthalene, anthracene, and their derivatives and analogous compounds—constitute a considerable portion of coal-hydrogenation products and accordingly have been of interest to those studying the destructive hydrogenation reaction.

Hall⁷⁰ has published a comprehensive investigation of the destructive hydrogenation of naphthalene along with a review of other work on the subject. It was found that, in a nickel-steel converter with a hydrogen pressure of 100 atmospheres, decomposition of naphthalene set in at temperatures of 450 to 475°C and became ap-

preciable only at 500°C . In the presence of 10 percent of active charcoal containing 13 percent of ammonium molybdate, naphthalene hydrogenated without rupture of the molecule to the extent of 30 percent at 350 and to over 90 percent at 400°C . At this temperature, cracking set in, became appreciable at 450, considerable at 475, and

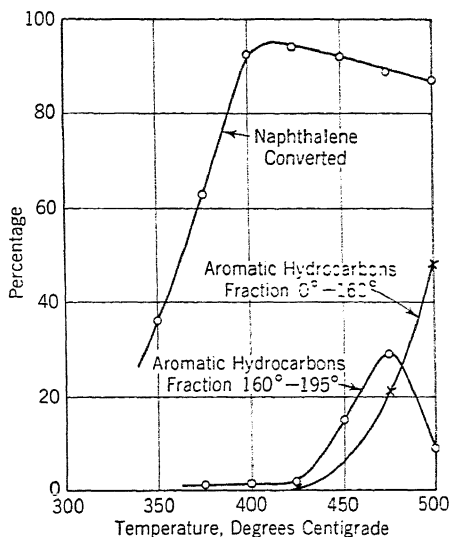


FIG. 21. Hydrogenation products from naphthalene.⁷⁰

at 500°C in 2 hours 50 percent of the original naphthalene was converted to hydrocarbons boiling below 160°C . Figure 21 shows the course of the destructive hydrogenation. The fraction boiling to 160°C contained cyclopentane, methylcyclopentane, cyclohexane and benzene, methylcyclohexane and toluene, ethylcyclohexane and ethylbenzene; the 160 to 195°C fraction contained some ethylbenzene but chiefly *n*-butylbenzene. The probable mechanism of the destructive hydrogenation of naphthalene is shown in Fig. 22.

The destructive hydrogenation of 1- and 2-methylnaphthalene and of 2,6-dimethyl-

⁷⁰ Hall, C. C., *Fuel*, **12**, 76-93 (1933).

CHEMICAL CONSTITUTION OF COAL

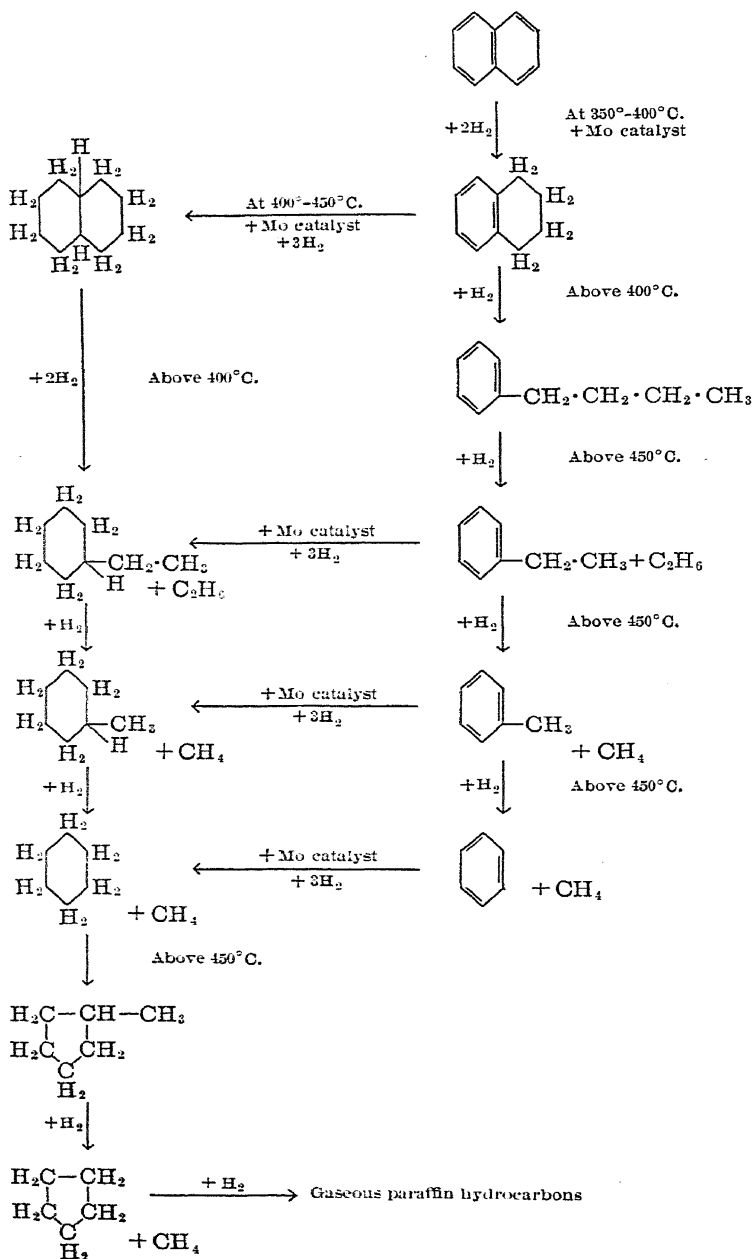


FIG. 22. Course of the destructive hydrogenation of naphthalene.⁷⁰

naphthalene proceeds⁷¹ like that of naphthalene. In the absence of catalyst little or no reaction takes place at 450° C. In the presence of a supported molybdenum sulfide catalyst, hydrogenation to the corresponding tetrahydromethylnaphthalene is almost complete at 400° C. Above 400° C, the tetrahydro product decomposes to form *m*- and *p*-alkyltoluenes. Demethylation of the methylnaphthalene and their tetrahydrides proceeds slowly at 450 and rapidly at 500° C.

In the destructive hydrogenation of indene,⁷¹ in the temperature range 300–500° C, from 30 to 50 percent of the material treated is converted into more complex products of polymerization and condensation, independently of the presence of a molybdenum catalyst. At the lower temperatures, truxene and liquid polymerides predominate; at the higher temperatures, resins and their decomposition products are formed. The behavior of the remaining 50 to 70 percent of the material treated is analogous to that of hydrocarbons of the naphthalene series. Hydroindene is formed and above 400° C is decomposed independently of the molybdenum catalyst, forming benzene hydrocarbons, principally toluene. The only observed effect of the molybdenum catalyst on the reactions of indene occurs at temperatures above 450° C; the polymerization of resins to pitch is inhibited, and stable, viscous oils are produced therefrom.

The destructive hydrogenation of oxygenated compounds also has been studied. It has been found that phenol⁷² and the cresols⁷³ in the absence of a catalyst are fairly stable at 450° C. The dihydric phenols⁷³ are much less stable, resorcinol being

partly, and hydroquinone completely, decomposed to carbon, pitch, and water at this temperature.

In the presence of a catalyst, commencing between 300 and 350° C and becoming rapid at 450° C, phenol and cresol are converted to neutral oils, mainly benzene and cyclohexane, and toluene and methylcyclohexane. The dihydric phenols behave differently. It appears that one or both of the hydroxyl groups break off under the action of heat alone, and the catalyst plays the secondary role of accelerating the hydrogenation of the resulting fragments to stable molecules. At 450° C in the presence of a good hydrogenating catalyst, the products are mainly benzene and cyclohexane; with a poor catalyst considerable pitch may be formed.

The naphthols,⁷⁴ which may be regarded as representative of a large group of higher-boiling phenols, occupy a position, with regard to stability, intermediate between that of phenol and the polyhydric phenols. Thus, at 450° C in the absence of a catalyst, condensation occurs, not to pitch and carbon but to dinaphthyl ethers and dinaphthalene oxide. In the presence of a molybdenum catalyst, the elimination of oxygen is practically complete at 400° C. The rate of hydrogenation is sufficient to prevent condensation, and the product consists mainly of naphthalene and tetralin.

Diphenylene oxide⁷⁵ is fairly stable at 500° C in the absence of a catalyst, and, even in the presence of supported molybdenum catalyst⁷⁶ at 450° C, 40 to 60 percent remains unchanged after 2 hours of heating. In the presence of a more active hydrogenating catalyst, such as pelleted molybdenum disulfide, only 14 percent re-

⁷¹ Hall, C. C., *J. Soc. Chem. Ind.*, **54**, 208–17T (1935).

⁷² Cawley, C. M., *Fuel*, **11**, 217–21 (1932).

⁷³ Cawley, C. M., *ibid.*, **12**, 29–35 (1933).

⁷⁴ Hall, C. C., *Fuel*, **12**, 419–27 (1933).

⁷⁵ Ogawa, T., *Bull. Chem. Soc. Japan*, **6**, 174–95 (1931).

⁷⁶ Hall, C. C., and Cawley, C. M., *J. Soc. Chem. Ind.*, **58**, 7–13T (1939).

mains after 2 hours at 450° C and 35 percent after 2 hours at 350° C. At low temperatures *o*-cyclohexylphenol and 2-phenylcyclohexanol are first formed and then deoxygenated to phenylcyclohexane. At higher temperatures, diphenyl is formed.

The benzenecarboxylic acids⁷⁷ are less stable than the phenols and are largely unaffected by the use of a supported molybdenum catalyst, the decarboxylation appearing to be a straight thermal decomposition.

These studies of the destructive hydrogenation of known compounds and the kinetics of the destructive hydrogenation of coal make it possible to associate certain types of chemical structures or groups of atoms with certain phases of the reaction of hydrogen with coal and the products thereof. Such inferences as can be drawn are summarized here as an aid in developing a picture of the nature of the chemical linkage of carbon, hydrogen, and oxygen in coal.

The primary liquefaction occurring below 370° C is in all probability a combination of solution and depolymerization of high-molecular-weight substances formed during coalification by condensation reactions or by polymerization of unsaturated structures resulting through loss of water in the coalification process.

Above 370° C the temperature coefficient of liquefaction shows such a high energy requirement for the reaction that the breaking of strong primary bonds, either carbon-to-carbon or carbon-to-oxygen or both, is indicated. In a substance which is almost entirely cyclic, breaking of carbon bonds resulting in marked reduction in molecular size would most likely be similar to the cleavage of diphenyl to form benzene.

The nature of the structures involved in the apparently strictly thermal decompo-

sition of the coal substance occurring just above 370° C, and resulting in the elimination of roughly 60 percent of the oxygen of the coal chiefly as carbon dioxide and water but partly as low-molecular-weight phenols, is not evident. The reaction is concomitant with and has the same temperature coefficient as the liquefaction reaction occurring in the same temperature range. The decomposition of carboxylic acids is strongly indicated as accounting for the carbon dioxide and a small portion of the water. The formation of low-molecular-weight phenols and the concomitance of the liquefaction and oxygen-removal reactions suggest the breaking of linear ether linkages. The cleavage of ring oxygen simultaneously with or followed by cleavage of carbon-to-carbon bonds is another possibility to account for low-molecular-weight phenols. The concomitance of liquefaction and oxygen-removal reactions may be a coincidence, and the elimination of water may be partly a continuation of the coalification process, that is, condensation to larger molecules or formation of unsaturated linkages. That liquefaction occurs in spite of this continuation of the coalification process means simply that the rate of cleavage of molecules overshadows the rate of condensation on the one hand and that the presence of hydrogen prevents polymerization of the unsaturates on the other hand.

The reaction eliminating the last 40 percent of the oxygen in coal is slower. This reaction is partly the deoxygenation of nonvolatile phenols formed simultaneously with the volatile phenols during the early stages of the oxygen-removal process. It is quite probable that additional phenols of both high and low molecular weights are formed during this later stage of oxygen removal.

The negative temperature coefficient of

⁷⁷ Cawley, C. M., *Fuel*, **12**, 366-70 (1933).

liquefaction at temperatures above 440° C is undoubtedly associated with polymerization reactions which lead, however, to other products than the original coalification process. In general, three sources of material susceptible of polymerization may be recognized: (1) products of the initial depolymerization of the coal substance, (2) unsaturated compounds formed by the elimination of water, and (3) the radicals formed by the high-temperature cracking reaction. Definite evidence of sources 1 and 2 is seen in the presence of material polymerized by the action of sulfuric acid in the products resulting from the hydrogenation of coal at temperatures as low as 350° C.

The evolution of gaseous hydrocarbons, particularly ethane, seems definitely associated with the hydrogenation cracking of cyclic hydrocarbons.

With the above inferences in mind, the carbon, hydrogen, and oxygen linkages in coal may be pictured as follows:

Plant life remains, composed of more or less highly oxygenated carbon compounds, have undergone a condensation process called "coalification." This condensation, involving the elimination of water and carbon dioxide, resulted in an essentially condensed polynuclear (five- and six-membered rings) carbon skeleton of high molecular weight. Various degrees of completion of this reaction have resulted in various sized units and in the retention of various amounts of oxygen, the smaller units containing the greater portion of the oxygen retained. The retention of highly reactive oxygen is facilitated by the immobilization of these groups in the highly viscous coalification product.

As the result of the various types of oxy-

gen in the original plant remains and the various degrees of coalification attained, the oxygen remaining in the coal is present in several forms. The last stage of condensation in which oxygen is retained finds the oxygen in the form of cyclic ethers (heterocyclic carbon-oxygen rings); that is, the condensed polynuclear skeleton has some rings in which carbon and oxygen atoms are present. Linear ethers may also result; i.e., two cyclic units may be held together by an oxygen atom only. As mentioned before, reactive oxygen such as hydroxyl, carbonyl, and carboxyl may be retained particularly in lower-rank coals. To complete the picture of the oxygen in coal it should be pointed out that oxidation during weathering subsequent to coalification may account for some of the reactive oxygen.

The unusual characteristics of some types of coal, such as cannel coal, are most probably the result of peculiar coalification conditions. Plant remains contain a certain percentage of polynuclear carbon units which are lower in oxygen than the other constituents. Complete oxidation of the more highly oxygenated constituents prior to extensive coalification should result in a coal of different type, one in which a lower content of oxygen may be associated with a lower average molecular weight, a relationship contrary to that experienced with most coals.

Owing to the high hydrogen-to-carbon ratio in the original plant remains, the hydrogen content of coal, even after far-reaching coalification, is considerably in excess of the requirements of a completely aromatic structure. Although some strictly paraffinic constituents exist in coal, much of the polynuclear ring structure must be saturated, i.e., hydroaromatic, or partially saturated, giving rise to olefinic double bonds. The paraffinic substances were probably constituents of the original plant remains which, because of their chemical inertness, persist as such in the coalification product.

CHEMICAL CONSTITUTION OF COAL: AS DETERMINED BY
HYDROLYTIC REACTIONS

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It appears probable that condensation reactions involving the elimination of water constitute an important part of the coalification process, and these reactions must be responsible in a considerable degree for the increasing molecular complexity observed as we pass from lower-rank carbonaceous materials, such as peat, to bituminous coal. One would therefore expect that wherever reversal of these condensations by hydrolytic reaction was possible there would result considerable degradation of the coal structure into simpler units. This point of view appears to be partly confirmed by the behavior of the lower-rank bituminous coals, but, with those of higher rank, reaction with such reagents as aqueous alkali at elevated temperatures seems to involve in addition to hydrolysis a "water-gas" reaction in which part of the carbonaceous material is oxidized to carbon dioxide and hydrogen is liberated.^{1, 2} Thus, with the higher-rank materials, oxidation and hydrogenation reactions may occur concomitantly with those of hydrolysis. Hydrolytic attack on synthetic linear polymers, such as the polyesters, polyamides, and polyhydrides, and on cellulose and the proteins results in high yields of

the simple building units. Hence, the failure of a high-molecular-weight body to be degraded into simpler units by hydrolysis is in itself a clue to structure, since it indicates the absence of readily hydrolyzable linkages such as ester, anhydride, and so forth, in other than peripheral positions. It is interesting to note in this connection that the action of aqueous alkali at elevated temperatures on a tridimensional synthetic substance, such as Bakelite, exhibits certain analogies to its action on the higher-rank coals, since reactions other than simple hydrolysis appear to be involved.³

With many organic structures hydrolysis in either acid or alkaline medium is effective. For coal, however, there are no data which indicate any hydrolytic breakdown in other than alkaline medium. Dilute hydrochloric or sulfuric acid appears to be without effect, at least up to temperatures which can be reached without pressure equipment. Nitric acid, even at concentrations as low as 1*N*, reacts fairly rapidly with bituminous coals of the rank of the Pittsburgh Seam coal, but the evidence indicates that the reaction is predominantly an oxidation.⁴

¹ Fischer, F., and Schrader, H., *Ges. Abhandl. Kenntnis Kohle*, **5**, 360-5 (1920).

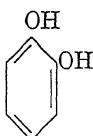
² Kasehagen, L., *Ind. Eng. Chem.*, **29**, 600-4 (1937).

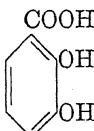
³ Allen, I., Meharg, V. E., and Schmidt, J. H., *Ind. Eng. Chem.*, **26**, 663-9 (1934).

⁴ Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **57**, 512-6 (1935).

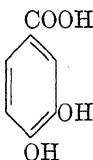
The action of alkali, of concentrations from 1 *N* to 100 percent, on a variety of coals and related materials, has been studied by a number of investigators. In the earlier work, where the reactions were carried out in open vessels, undoubtedly some atmospheric oxidation accompanied the other reactions.

Characteristic products from the action of fused alkali, probably 90 percent concentration, on peat, lignites, and humic

acids are: catechol, , pyrocate-

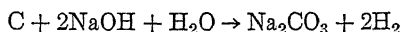
chuic acid, , oxalic acid, and the

lower fatty acids. The isolation of 3,4-di-

hydroxybenzoic acid, , has also

been reported from the alkali fusion of natural humic acids.⁵

Early investigations dealing with the action of alkali on higher-rank carbonaceous materials were carried out in connection with a controversy over the reaction mechanism of the Jacques fuel cell. Haber and Bruner⁶ showed that wood charcoal, coke, graphite, and "pure carbon" reacted with sodium hydroxide at 350° C according to the following equation:



⁵ Strache, H., and Lant, R., *Kohlenchemie*, Akademische Verlagsgesellschaft, Leipzig, 1924, pp. 286-7.

⁶ Haber, F., and Bruner, L., *Z. Elektrochem.*, **10**, 697-713 (1904).

Wood charcoal and graphitic are light carbons were found to dissolve in a boiling solution of sodium hydroxide with the formation of carbonate and the evolution of hydrogen. LeBlanc⁷ showed that carbon prepared by the action of sodium on carbon dioxide furnished hydrogen at 650° C when fused with potassium hydroxide. Reaction with diamond required⁸ a much higher temperature, 1,200° C.

In more detailed investigations, Donath and Bräunlich⁹ studied the action of fused alkali on brown and bituminous coals. The experiments were carried out in an open silver dish, and there was undoubtedly a considerable amount of atmospheric oxidation. Under these conditions it was found, as would be expected, that the lower-rank materials were rapidly converted to brown, alkali-soluble products. The bituminous coals were found to be attacked much more slowly but could be dissolved completely by repeated action at 400° C.

Fischer and coworkers carried on a series of investigations dealing with the action of alkali on various coals and derived products. As all the work was in closed systems, atmospheric oxidation could not have been an important factor. The action of 5 *N* sodium hydroxide at 250° C on a "Lohbergkohle" was found¹⁰ to yield about 2.5 percent of the weight of the coal as alkali-soluble products. The whole mass of the coal was greatly altered; it was found to have developed plastic properties and caked together to form coke. Later work¹¹ on the same coal at higher tem-

⁷ LeBlanc, M., and Weyl, O., *Ber.*, **45**, 2300-15 (1912).

⁸ Moissan, H., *Compt. rend.*, **116**, 460-3 (1893).

⁹ Donath, E., and Bräunlich, F., *Chem.-Ztg.*, **36**, 373-6 (1912).

¹⁰ Fischer, F., and Glud, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 243-5 (1918).

¹¹ Fischer, F., and Schrader, H., *ibid.*, **5**, 353 (1920).

peratures, 300° C, with 4.1 *N* potassium hydroxide, showed that 21 percent of this coal could be converted to alkali-soluble products, of which 75 percent precipitated on acidification, indicating phenolic or acidic products. Volatile acids to the extent of 47 milliequivalents per 100 grams of coal were found, and a small part of these was characterized as formic acid.

More detailed investigations were made by Fischer and Schrader^{11, 12} on brown coal and on "Union" briquets. Three types of reaction were definitely recognized as taking place: hydrolysis; oxidation by the water with carbon dioxide formation and hydrogen evolution; and hydrogenation. With 10 *N* potassium hydroxide at temperatures from 276 to 284° C, about 75 percent of the briquet material was made alkali soluble. Of the part insoluble in alkali, about a half was soluble in alcohol. Approximately 25 percent, based on the weight of the briquets of the alkali-soluble material, was found to consist of ether, alcohol, or water-soluble products. Catechol and catechuic acid were definitely identified among them.

In an investigation of the action of aqueous alkali on lignin¹² it was found that, in 2.5 percent sodium hydroxide at 200° C, the methoxyl groups were stable; at 300°, hydrolysis was nearly complete, indicating that, with these simple ether linkages, alkali treatment at elevated temperatures is a very effective splitting agent.

More recent work where nonaqueous solutions of alkali have been employed has indicated the very interesting possibilities in this little-investigated field. Withrow and Pew¹³ extracted a sample of Pittsburgh Seam coal with a 1 *N* solution of

potassium hydroxide in the monomethyl ether of ethylene glycol. The temperature was not stated, but presumably it was close to the normal boiling point of the pure solvent, 132 to 135° C. The weight of the residue was 70.5 percent of the original coal. A similar extraction with 10 percent aqueous sodium hydroxide at its boiling point gave 97.5 percent residue, and with the pure monomethyl ether of ethylene glycol a residue of 90.0 percent was obtained. The superiority of the combination of the alkali and the organic solvent is obvious. In view of the well-known effectiveness of combinations of organic solvents and alkali in hydrolytic reactions, it appears that this field is well worth further investigation.¹⁴

Kasehagen² has studied the action of sodium hydroxide on a Pittsburgh Seam coal over the temperature range 250 to 400° C. The reaction was carried out in a nickel-lined autoclave, and the alkali concentrations ranged from 1 *N* to 100 percent. The alkaline solution recovered was first extracted with benzene to remove neutral oils. It was then acidified, and the precipitated phenols and acids were separated by filtration, the amount of carbonate formed being determined in an aliquot before this acidification step. Further amounts of acidic materials were recovered by solvent extraction of the filtrate, from the phenol and acid separation, and from the solid residue obtained on its evaporation. The amount of material recovered by these last-named procedures was found to be small and it was not characterized other than to establish its acidic reaction.

The data are summarized in Table I and in Figs. 1 and 2. The maximum yield of alkali-soluble products was obtained with

¹² Fischer, F., and Schrader, H., *ibid.*, **5**, 332-65 (1920).

¹³ Withrow, J. R., and Pew, J. C., *Fuel*, **10**, 44-7 (1931).

¹⁴ E.g., alcoholic alkali. Also see work in diphenyl ether by Huntress, E. H., and Seikel, M. K., *J. Am. Chem. Soc.*, **61**, 816-22 (1939).

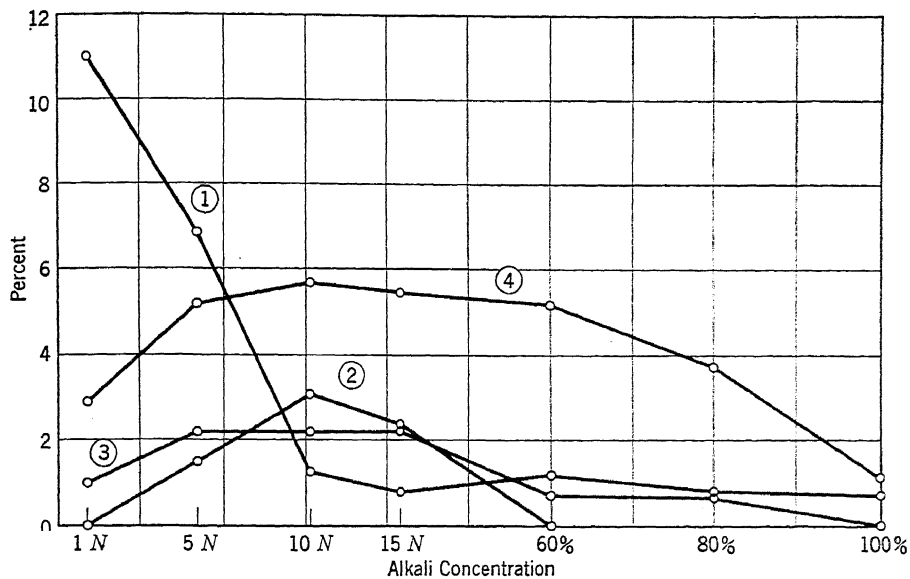


FIG. 1. Distribution of carbon in products from runs at 250°C.: (1) Phenols and acids; (2) neutral oil; (3) hydrocarbon gases; (4) carbon dioxide.

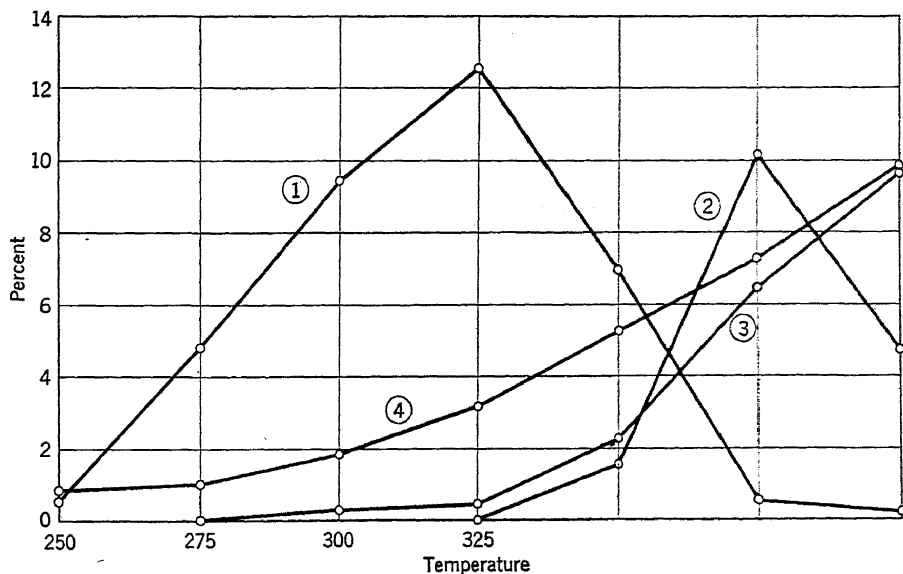


FIG. 2. Distribution of carbon in products from runs with 5 N sodium hydroxide.: (1) Phenols and acids; (2) neutral oil; (3) hydrocarbon gases; (4) carbon dioxide.

TABLE I

ACTION OF ALKALI ON PITTSBURGH SEAM COAL²

Experi- ment No.	Tem- perature °C	Alkali Concen- tration	Pressure pounds per square inch	Distribution of Carbon in Products				
				Residue percent	Phenols and Acids percent	Neutral Oil percent	Hydro- Carbon Gases percent	Carbon Dioxide percent
1	250	5N	450	96.5	0.5		...	0.8
2	275	5N	800	91.9	4.8		...	1.0
3	300	5N	1,300	86.0	9.4		0.2	1.8
4	325	5N	1,750	78.8	12.5		0.4	3.1
5	325	60%	600	89.5	0.9		0.8	3.5
6	350	1N	2,500	81.2	11.0		1.0	2.9
7	350	5N	2,550	77.4	6.9	1.5	2.2	5.2
8	350	10N	2,400	80.9	1.3	3.1	2.2	5.7
9	350	15N	1,900	83.0	0.8	2.4	2.3	5.5
10	350	60%	700	87.5	1.2	...	0.7	5.2
11	350	80%	250	94.4	0.8	0.1	0.8	3.7
12	350	100%	92.7	0.7	1.1
13	375	5N	3,600	74.0	0.5	10.1	6.4	7.2
14	400	5N	4,300	72.3	0.2	4.7	9.6	9.8
15	400	60%	1,350	81.1	0.7	0.9	4.1	7.1

rather dilute alkali, 1 N and 5 N, at temperatures of 350 and 325° C. The rapid decrease in alkali-soluble material above this temperature range, coincident with increase in the amount of neutral oils, suggests that these resulted at least in part from reaction of the alkali with the phenols and acids. The relatively small yield of alkali-soluble degradation products and the large fraction of insoluble residue indicate the absence, in this coal, of any considerable amount of linkages hydrolyzed under these conditions.

The alkali-soluble material was shown to be predominantly phenolic, 95 percent, by "springing" from the alkaline solution with carbon dioxide and by methylation with dimethyl sulfate in the presence of alkali. A typical sample was of the following composition: C 80.04, H 5.30, N 1.53, S 1.16, and O (by difference) 11.97 percent. The molecular weight determined cryoscopy-

cally in catechol was 219. The combining weight calculated from the methoxyl content was 226. The oxygen content shown by the ultimate analysis indicates the presence of roughly one oxygen atom per molecule in other than a functional group. This observation is of interest in connection with the postulation^{15, 16} of the presence of two different types of oxygen in bituminous coal.

Although the amount of alkali-soluble degradation products formed by the reaction in alkali did not constitute an important part of the coal in the work of Kasehagen, there was evidence that some deep-seated change, not manifesting itself in alkali solubility, had taken place, for by

¹⁵ Fisher, C. H., and Eisner, A., *Ind. Eng. Chem.*, **29**, 1371-6 (1937).

¹⁶ Erasmus, Paul, *Über die Bildung und den chemischen Bau der Kohlen*, Enke, Stuttgart, 1938, p. 10. Also see Fuchs, W., *Die Chemie der Kohle*, Julius Springer, Berlin, 1931, pp. 325-6.

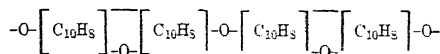
exhaustive extraction of the residue with benzene, in a Soxhlet, a benzene-soluble material containing 26.8, 21.5, 27.3, and 23.1 percent of the carbon in the coal was obtained in runs 5, 9, 10, and 11, respectively. Similar benzene extractions of the original coal gave 6 to 8 percent. Whether the benzene-soluble material was a hydrogenation product, formed by active hydrogen furnished by a water-gas reaction, or a hydrolytic breakdown product of a molecular weight such that it was insoluble in alkali in spite of the presence of some hydroxyl groups, cannot be decided from the data available.

The development of plasticity, which was noted by the earlier workers¹⁰ as well as by Kasehagen, so far below the normal plastic range of this coal, was due, it appears probable, to incipient hydrogenation reactions on the surface of the particles.

Later experiments¹⁷ carried out with a similar technique on an Illinois No. 6 Seam bituminous coal showed over 30 percent of the carbon of this coal to be convertible to phenolic and acidic products, compared with about 12 percent for the Pittsburgh Seam coal. The much greater amenability of the lower-rank coal to alkaline hydrolytic decomposition is evident, and further investigation of the nature of the products produced would be of great interest.

In 1938 there appeared a posthumous monograph¹⁶ describing the work of Erasmus in Bergius's laboratory and containing an important section dealing with the hydrolysis of bituminous coal. The point of view developed was that coal consists of a tridimensional type of polymer of relatively small aromatic and hydroaromatic units, of ten carbon atoms each, linked through linear and cyclic ether oxygen bonds, and that the principal mass of the

coal is essentially unitary. Resins, waxes, coloring materials, cuticles, and so forth, were specifically excluded from the discussion, and the findings were stated to apply chiefly to the bright coals as opposed to the durains. Hydrolytic reactions, carried out in aqueous alkali at elevated temperatures, were described, and the effectiveness of alcoholic solutions of alkali at moderate temperatures, especially those containing small amounts of alkali alcoholates, was pointed out. A typical coal structure was pictured as follows:



From such a molecular structure, if complete hydrolysis of both linear and cyclic ether bonds took place, one would expect units containing twenty carbon atoms with three or four hydroxyl groups attached to each, depending on which side of the linear ether bond hydrolysis took place. It was stated that fragments of this type were found.¹⁸ It was admitted, however, that whereas the first step in the hydrolysis, which was assumed to be the opening of the cyclic ether structures and which did not effect significant changes in molecular weight, occurred readily, the second step, the breaking of linear ether bonds, which was necessarily accompanied by marked changes in molecular weight, took place with great difficulty, conversions being usually 30 to 40 percent and only rarely 60 to 80 percent. The difficulty of the hydrolysis of the linear linkages compared, for example, with that of cellulose was ascribed to the hindering effects accompanying a network type of high-molecular-

¹⁸ They were described as $C_{10}H_8$ units with two or three hydroxyl groups. It is not obvious how the carbon-to-carbon linkage was broken.

¹⁷ Unpublished data, Coal Research Laboratory.

weight body as compared with a linear structure like cellulose. Crystalline material was obtained by the bromination of the water-soluble hydrolytic products, but no compounds were isolated. No data were

included in this monograph, and none have been published, but the point of view developed is of such interest as to suggest the importance of further investigations in the field of hydrolytic reactions on coal.

CHAPTER 12

FORMS OF SULFUR IN COAL

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Sulfur is an undesirable but economically important constituent of all coals. It is present in amounts ranging from traces to as high as 10 or more percent, commercial coals, however, rarely containing more than 5 percent. The great bulk of the commercial coals of the Eastern United States contains from 0.5 to 1.5 percent of sulfur. Charts have been prepared¹ which indicate the properties of coal which are of importance for the various applications to which coals may be put, including the factors of total sulfur and the forms of sulfur. Kreisinger² also has discussed the significance of sulfur in coal from the viewpoint of the consumer who uses coal as fuel.

According to the Consumers' Counsel of the National Bituminous Coal Commission,³ "Sulfur is found in all coals, but ordinarily is of little importance to the domestic consumer except where it is found in amounts so great as to constitute a health hazard in improperly constructed furnaces. Moisture and sulfur contents are an indication of liability of the coal to spontaneous combustion during storage. These factors should be considered by the consumer who

intends to buy his winter supply in the summer."

The extent of the sulfur dioxide pollution of the air over the city of Chicago and vicinity, which resulted largely from the combustion of bituminous coal, has been reported by Singh,⁴ who stated that the obvious remedy would be the reduction of sulfur in the coal at the mine by coal-preparation processes. The subject of sulfur in coal as a nuisance has often been discussed in the literature.⁵

OCCURRENCE OF SULFUR IN COAL

Sulfur does not occur as such in coal but is present in organic combination as part of the coal substance and in inorganic combination as pyrite or marcasite and, especially in weathered coals, as calcium sulfate. These forms of sulfur are commonly referred to as organic, pyritic, and sulfate sulfur. In coke, sulfur occurs in organic combination and as sulfides.

Organic sulfur is distributed throughout the coal substance and cannot be removed by mechanical cleaning or preparation

¹ *Natl. Com. on Coal, Natl. Assoc. Purchasing Agents, Rept. 21*, 2nd ed., 1936, 21 pp.

² Kreisinger, H., *Proc. Am. Soc. Testing Materials*, **37**, II, 369-72 (1937).

³ Consumers' Counsel of the Natl. Bituminous Coal Commission, *Consumer Ideas* **3**, Supt. of Documents, Washington, D. C., 1938.

⁴ Singh, A. D., *Univ. Illinois Eng. Expt. Sta., Circ. 36* (1939), 32 pp.

⁵ Himus, G. W., and Egerton, A. C., *Proc. 3rd Annual Conf. Combustion Appliance Makers Assoc.*, **1939**, 87-97. Armstrong, V., and Himus, G. W., *Chemistry & Industry*, **1939**, 543-S. Burdick, L. R., and Barkley, J. F., *U. S. Bur. Mines, Information Circ. 7066* (1939), 14 pp.

processes. Cady⁶ has stated that "There has been no determination of the nature of the distribution of the organically combined sulfur among the plant constituents of Illinois coal, although it is probable that certain constituents will contain more sulfur than others. This is a matter suitable for investigation, but in the meantime the organic sulfur must be regarded as homogeneously combined with the coal material."

Organic sulfur does not intrude its presence on the observer as does pyrite, yet even the early investigators recognized that some of the sulfur in coal must be present in some other form than as inorganic compounds and surmised that it was present in the organic matter making up the coal.⁷

Though no definite rule can be established, in general the sulfur content of low-sulfur coals is usually largely organic. The organic sulfur content of coals of increasing total sulfur content tends to increase, but the pyritic sulfur tends to increase at a greater rate and to make up a greater proportion of the total sulfur. Yancey and Fraser⁸ found no relationship between the organic and pyritic sulfur contents of the coals they studied. One remarkable bituminous coal having the very high sulfur content of almost 10 percent—the Arsa coal of Istria—has been reported to contain about 1 percent of pyritic sulfur, almost 8 percent organic sulfur, and practically no sulfate sulfur.⁹

The nature of organic sulfur compounds

in coal is unknown. Strache and Lant¹⁰ stated that even less is known about them than about the nitrogen compounds in coal. Further, according to Stopes and Wheeler,¹¹ "We do not know whether the sulfur-containing organic compounds are simple or complex in structure, or whether, as is possible, the majority or all of the complex molecules that form the coal conglomerate possess each a sulfur atom in some grouping in their structure." They stated also that the latter hypothesis is supported by the fact that all extracts from coal except possibly resins contained sulfur, and that all nitroulmins from coal contained sulfur. Wheeler¹² found that all natural ulmins, whether from peat or coal, contained nitrogen and sulfur. Because the pyridine and chloroform extracts and the extraction residue all had the same sulfur content as the original coal, Wheeler¹³ concluded that the organic sulfur compounds were part of the fundamental constitution of coal and were uniformly distributed.

Postovskii and Harlampovich¹⁴ synthetically sulfureted coal by treatment with sulfur and found the coal to be then less reactive to sulfur monochloride, indicating a vulcanization. From the behavior of these synthetically sulfureted coals, they attempted to draw conclusions as to the sulfur contents of coal. The presence of thioether linkages in coals was detected by the methyl iodide reaction, and such linkages were estimated by them to account

⁶ Cady, G. H., *Illinois State Geol. Survey, Bull.* **62**, 37 (1935).

⁷ Wormley, T. G., *Ohio Geol. Survey, Rept. Progress*, 1869, 110-2, 1870, 142. Wallace, W., *Chem. News*, **41**, 201 (1880). Muck, F., *Stahl u. Eisen*, **6**, 468-73 (1886).

⁸ Yancey, H. F., and Fraser, T., *Univ. Illinois, Eng. Expt. Sta., Bull.* **125** (1921), 94 pp.

⁹ Donath, E., and Indra, A., *Chem.-Ztg.*, **36**, 1118-20 (1912). Fischer, F., *Ges. Abhandl. Kenntnis Kohle*, **3**, 98-101 (1918).

¹⁰ Strache, H., and Lant, R., *Kohlenchemie*, Akademische Verlagsgesellschaft, Leipzig, 1924, p. 249.

¹¹ Stopes, M. C., and Wheeler, R. V., *Fuel*, **3**, 131-2 (1924).

¹² Wheeler, R. V., *Chemistry & Industry*, **1926**, 335-44.

¹³ Wheeler, R. V., *Colliery Guardian*, **121**, 1596-7 (1921).

¹⁴ Postovskii, I. Y., and Harlampovich, A. B., *Fuel*, **15**, 229-32 (1936).

for 18.3, 20.4, and 32.1 percent of the total sulfur content of three coals they investigated.

Powell and Parr¹⁵ distinguished between phenol-soluble or resinic sulfur and phenol-insoluble or humic sulfur on the basis of the organic sulfur content of the phenol-soluble and -insoluble portions of coal. Wheeler¹³ attached no significance to this distinction. Petrascheck¹⁶ pointed out that beds with marine cover have higher sulfur contents and, further, that often it is found that higher organic sulfur content accompanies better coking properties in a series of coals.

Pyritic sulfur is extremely variable in its occurrence in coals, both in amount and form. "It may occur as horizontal layers in the coal bed; as fillings in the vertical cleat cracks or joints; as nodular masses parallel with or at an angle to the bedding; as fillings in the desiccation cracks, the fusain and resin rodlet cavities more commonly occupied by calcite and kaolinite; as minute aggregates scattered irregularly through the various lithologic ingredients of the coal, especially within vitrain bands; and as intimate mixtures with and impregnations of certain parts of the coal such as the fusain walls."¹⁷ R. Thiessen¹⁸ found that all coals examined by him contained very small globules or particles of pyrite varying in diameter from a few microns to a hundred microns. Pyrite is found in coal in particles from microscopic sizes on up to large masses or

boulders several feet or more in diameter and in definite widely extending bands in the bed up to almost a foot in thickness. The finely disseminated pyrite may form thin filmlike coatings on the joint planes, giving the natural cleavage face of a lump of coal the appearance of having been gilded. In this form, a fraction of a percent of sulfur may make the coal appear very dirty and contaminated. Fusain is frequently thickly impregnated with pyrite.

Coarser pyrite occurs in lens-shaped masses ranging in size from very small particles up to lenses 3 or 4 feet thick and several hundred feet in diameter and may frequently be found in some beds up to 3 inches in thickness and about 1 foot in diameter. The larger masses are usually found towards the top or the bottom of the bed. Coal balls, or niggerheads, are frequently very rich in pyrite and may sometimes be almost pure, crystalline pyrite. The larger balls are usually found in the roof of the bed.

Larger and more massive occurrences of pyrite are frequently contaminated with shale, clay, and carbonaceous material and may contain well-preserved plant fossils. Preserved pyritized vegetable fossils are not uncommon, although they do not constitute any considerable part of pyrite.⁸ Macpherson, Simpkin, and Wild¹⁹ have classified pyrites as crystalline, massive, nodular, stringy, granular, and globular and have presented excellent reproductions of photographs of these types of pyrite. They also reported analyses of specimens of several varieties of coal pyrite. The manner of occurrence and the possible origin of pyrite in Illinois coals have also been discussed and illustrated by Holbrook.²⁰

¹⁵ Parr, S. W., and Hadley, H. F., *Univ. Illinois, Eng. Expt. Sta. Bull.* 76 (1914), 41 pp. Powell, A. R., and Parr, S. W., *ibid.*, 111 (1919), 66 pp.

¹⁶ Petrascheck, W., *Entstehung, Veredlung und Verwertung der Kohle*, Gebrüder Borntraeger, Berlin, 1930, pp. 20-1.

¹⁷ Ball, C. G., *Illinois State Geol. Survey, Rept. Investigations*, 33, 29 (1935).

¹⁸ Thiessen, R., *Trans. Am. Inst. Mining Met. Engrs.*, 63, 913-26 (1920).

¹⁹ Macpherson, H., Simpkin, S. N., and Wild, S. V., *Safety in Mines Research Board (London), Paper* 26, 24 pp.

²⁰ Holbrook, E. A., *Univ. Illinois, Eng. Expt. Sta., Circ.* 5 (1917), 46 pp.

Sulfate sulfur is generally interpreted to mean sulfur existing as calcium sulfate, although in badly weathered exposures it may also occur as ferrous sulfate. Unweathered coals contain only traces of sulfate sulfur, and its presence is an almost certain indication that the coal has been weathered.

ORIGIN OF FORMS OF SULFUR IN COAL

The organic sulfur of coal has its most probable origin in the sulfur in the coal-forming plants.¹² Stopes and Wheeler¹¹ stated that the findings of Yancey and Fraser⁸ that there was no relationship between the amounts of pyritic and organic sulfur found in coals support the belief that much of the sulfur in coal is derived from the original sulfur-containing compounds in the plants from which the coal was formed. Sulfur is one of the essential elements of present-day plants and presumably also of all coal-forming plants. Dieulaufait²¹ investigated modern members of the Equisetaceae family, a family of important coal-forming plants, and found greater amounts of sulfur and lower amounts of carbonates in their ashes than in the ashes of other plants; he concluded that, as these plants contained more sulfur than other plants, their palaeozoic ancestors did also, an idea which has persisted.

Sulfur occurs in plants as a constituent of proteins and of certain waste and protective substances, especially in seeds, as, for example, the mustard oils and their glucosides.^{22, 23} During the decay of the plants in the bog, protein sulfur compounds are presumably quickly destroyed and

much sulfur is released as hydrogen sulfide. Part of this escapes to the atmosphere and part dissolves in the bog water, where it may combine with dissolved iron compounds or be washed away or absorbed by the organic coal-forming materials.

Because of the small percentage of the annual vegetation which finally enters into coal formation, the organic sulfur found in the coal must of necessity be only a small percentage of the sulfur in the annual increment of vegetation. It has also been suggested that part of the organic sulfur in coal may be derived from the residues of animal life which lived in the decaying peat bog. Such residues are rare and probably of minor account; in any event they would be similar in nature to the organic sulfur from the plants.²⁴ The pyrolytic decomposition products of coal gave little clue to the compounds in which the sulfur exists in coal.

PYRITIC SULFUR

The origin of pyrite in coal is a matter of much speculation, possibly because it appears probable that pyrite may have been formed in coal in several different ways and at different periods in the history of the coal bed. Theories have been advanced attributing pyrite to both external and internal sources of sulfur. Hydrogen sulfide, evolved through decay of the peat bog, can precipitate iron sulfide by reaction with soluble iron compounds, for example, iron carbonates present in the percolating ground waters. The ferrous sulfide first precipitated is later transformed to pyrite.¹³

Feld²⁵ found that iron bisulfides formed when ferrous sulfide and sulfur were warmed together in aqueous suspension, the

²¹ Dieulaufait, M., *Compt. rend.*, **100**, 284-6 (1885); *Eng. Mining J.*, **41**, 264 (1886). Anon., *Berg- u. hüttenmann. Z.*, **45**, 276 (1886).

²² Muhlert, F., *Der Kohlenschwefel*, Knapp, Halle, 1930, p. 1.

²³ Erdmann, E., and Dolch, M., *Die Chemie der Braunkohle*, Knapp, Halle, 2nd ed., 1927, p. 39.

²⁴ Potonié, H., *Die Entstehung der Steinkohle*, Gebrüder Borntraeger, Berlin, 5th ed., 1910, 225 pp.

²⁵ Feld, W., *Z. angew. Chem.*, **24**, 97-103 (1911).

conversion taking place under acid conditions but being hindered by basic conditions. It is well known that with certain forms of cover—for example, limestone—the coal in the same seam will have a lower sulfur content, particularly pyritic sulfur content, than the coal under a shale cover. Pyrite is readily formed by the action of hydrogen sulfide on iron in the presence of decaying organic matter, and the formation of pyrite tubes around rootlets which have grown in loess soil may be a relatively rapid process.

It has also been proposed that pyrite in coal has formed as a result of the reduction by the organic matter in the peat or coal bed of iron sulfate present in percolating waters. According to Bischoff,²⁶ one of the early investigators in this field, pyrite always forms when a suspension of sulfate salts and iron compounds comes in contact with decaying organic matter. According to this theory, it is not necessary for the iron to be in the dissolved form. The reduction of ferrous sulfate present in percolating waters would explain the thin coatings of pyrite on coal at shrinkage cracks. Ogura and Matsumoto,²⁷ discussing the occurrence of pyrite nodules in a Manchurian coal underlying rocks of marine origin, considered the iron to have come from the underlying rocks and the sulfur from the organic matter in the coal bed.

Sulfur bacteria²⁸ and iron bacteria²⁹ also may play an important role. The finely

disseminated pyrite granules distributed throughout the mass of coal and found extensively in the residues of woody components are probably the result of the activities of bacterial colonies. Such colonies are present in peat, and corresponding structures are found in coal of all ranks.¹⁵

White³⁰ attributed the high percentage of sulfur in the "interior basin" coals of the United States to the submergence of the peat-forming deposits under sea water, the immediate occupation of the area by animal life, and the action of sulfur bacteria. He further attributed the high sulfur contents of the coal of certain basins to the erosion of richly sulfide-bearing rocks in the basin drainage, and that of shallowly covered coal to secondary enrichment by sulfate-bearing waters from overlying strata.

Sulfur balls and lenses were obviously formed in the early stages of coal formation since the surrounding coal subsequently became compacted to a smaller thickness than the pyrite mass.

The pyrite filling joint cracks and other vertical and horizontal partings is probably of secondary origin and formed largely since the consolidation of the bed to approximately its present thickness. The lateness of its origin is indicated particularly by the lack of evidence of differential shrinkage between the coal and the pyrite which would be inevitable if it had formed at an early stage.³¹ Newhouse³² considered that globular concretions of iron sulfides in rocks other than coal are probably pyrite and are of syngenetic origin from gels which later crystallized, while the

²⁶ Bischoff, G., *Elements of Chemical and Physical Geology*, The Cavendish Society, London, 1854, Vol. 1, p. 163.

²⁷ Ogura, T., and Matsumoto, H., *Mem. Ryojun Coll. Eng.*, 1934, 243-55; *Chem. Abs.*, 29, 2484 (1935).

²⁸ Lafar, F., *Technical Mycology*, Griffin, London, 1910, 2 vols., 870 pp.

²⁹ Harder, E. C., *U. S. Geol. Survey, Professional Paper 113* (1919), 89 pp.

³⁰ White, D., Thiessen, R., and Davis, C. A., *U. S. Bur. Mines, Bull.* 38, 34-58 (1913).

³¹ Cady, G. H., *Illinois State Geol. Survey, Rept. Investigations* 35, 36 (1935).

³² Newhouse, W. H., *J. Geol.*, 35, 73-83 (1927).

iron sulfide forming bands and lenses in coal is probably marcasite deposited as a gel. The pyrite and marcasite formed later in the process of coalification and found along joints is more coarsely crystalline. Schwartz³³ found well-preserved plant structures by means of polished sections in rounded concretions of sulfides which were mainly pyrite obtained from Illinois coals.

SULFATE SULFUR

The presence of sulfate sulfur in a bituminous coal is certain evidence that these coals have been subjected to a weathering process since their formation. Freshly mined bituminous coal from beds which have never been uncovered after their formation or subjected to the action of oxygen-bearing percolating waters are practically free from sulfates. When sulfate sulfur is present it occurs as calcium sulfate and, in regions of rapid weathering of coals rich in pyrite, as ferrous sulfate. Because of the solubility of ferrous sulfate, percolating ground waters tend to remove it almost as fast as it is formed by the oxidation of pyrite. Through hydrolysis these waters deposit iron hydroxides and become highly acid. This condition is especially noticeable in the drainage from mines, especially side-hill mines which have been abandoned. Leitch³⁴ found that the drainage from mines containing high-pyritic coal was much more acid than that from mines of low or medium sulfur content. Of thirty-nine mines in Pennsylvania the drainage waters of twelve had a total acidity of 26 to 500 parts per million; three of 500 to 1,000; twenty-two of more than 1,000, mostly 1,500 to 3,000; and one almost 14,000 parts per million.

DETERMINATION OF THE SULFUR CONTENTS OF COALS

Coals are analyzed to determine their total sulfur content and the content of sulfate, pyritic, and organic sulfur. In addition, methods have been proposed for the determination of so-called combustible sulfur and noncombustible sulfur, which are, respectively, the sulfur which passes off with the flue gases on the combustion of coal and the sulfur which remains in the ash. Coke is analyzed to determine its total sulfur content, and it may also be analyzed to determine sulfide and organic sulfur contents.

METHODS OF ANALYSIS

Total Sulfur. Methods for the analysis of total sulfur in coal are based upon the combustion of the coal and retention of the sulfur oxides, their complete oxidation to the sulfate stage, and subsequent estimation. The generally accepted methods in use in the United States are those promulgated by the American Society for Testing Materials.³⁵ These methods include three procedures for the determination of total sulfur in coal or coke:

1. In the Eschka method, the coal is ignited with Eschka's mixture, a mixture of 2 parts by weight of light calcined magnesium oxide and 1 part of anhydrous sodium carbonate. After ignition, the residues are leached with hot water. The leachings are treated with bromine water to complete the oxidation of sulfur compounds to sulfate and acidified with hydrochloric acid, and the sulfate precipitated as barium sulfate, in which form it is weighed. This method is generally considered the most reliable.

³³ Schwartz, G. M., *ibid.*, 35, 375-7 (1927).

³⁴ Leitch, R. D., *U. S. Bur. Mines, Rept. Investigation* 3146 (1932), 15 pp.

³⁵ Am. Soc. Testing Materials, Method D271-37, *Am. Soc. Testing Materials, Standards*, 1939, Pt. 3, pp. 24-7. Am. Standards Assoc., Method K18.

2. In the bomb-washing method, the washings, collected during the calorimetric determination using the oxygen bomb calorimeter and after titration to obtain the acid correction, are made alkaline with ammonia, heated to boiling, filtered, treated with bromine water, and finally with barium chloride as in the Eschka method.

3. In the sodium peroxide fusion method, the coal is oxidized in a Parr coal sulfur bomb by means of sodium peroxide and potassium perchlorate or potassium chlorate. The oxidation residues are digested with water, acidified, and filtered, and the filtrate is treated with barium chloride as in the Eschka method.

These methods are the same as those used by the U. S. Bureau of Mines.³⁶ The Eschka and sodium peroxide methods are also standard methods of the United States Steel Corporation.³⁷ The three methods have been extensively studied, and the bomb-washing and peroxide methods have been found to check closely enough to the Eschka method to be considered alternatives.³⁸

Šimek, Ludmila, and Stanclova³⁹ compared the A.S.T.M., Eschka, Parr, and Stadnikoff-Titov modifications of the Eschka methods, found the Parr method the highest, and recommended the Stadnikoff-Titov modification over the conventional Eschka procedure.

³⁶ Stanton, F. M., Fieldner, A. C., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper 8* (1939), 59 pp.

³⁷ Chemists' Committee, United States Steel Corporation, *Sampling and Analysis of Coal, Coke, and By-products*, Carnegie Steel Company, 3rd ed., 1929, pp. 77-80.

³⁸ Selvig, W. A., and Fieldner, A. C., *Ind. Eng. Chem.*, **19**, 729-33 (1927); *Fuel*, **7**, 83-9 (1928). Nikolai, H. A., and Vorobyev, H., *Izvest. Teplo-tekhn. Inst.*, **1929**, No. 3, 91-2. King, J. G., and Crossley, H. E., *Fuel*, **8**, 544-8 (1929).

³⁹ Šimek, B. G., Ludmila, J., and Stanclova, B., *Mitt. Kohlenforsch. Inst. Prag*, **2**, 48-52 (1935).

Fischer,⁹ investigating the Arsa coal which is abnormally high in sulfur, particularly in organic sulfur, found that the Eschka method gave results several percent too low compared with the Carius method. He said this should have been expected since it was not reasonable to assume that the Eschka mixture would hold back and absorb the sulfur present in the tars and gases formed when the coal was heated in the Eschka sulfur determination.

As the sulfur content of coal is of considerable commercial importance, much attention has been given to methods for its estimation, especially toward ways of simplifying the methods or shortening the time required for the analysis. Many of these proposals have as their purpose the shortening of the overall time required to run a determination by the Eschka method either by decreasing the time required for the ignition or by eliminating the gravimetric procedure for the determination of the sulfate formed. Although some of these methods may shorten the elapsed time required for a determination, they require individual attention to each run and, therefore, are not attractive to a commercial or preparation plant laboratory where a large number of determinations have to be run during the day. In spite of all the proposed modifications, the Eschka and bomb-washing procedures as described by the A.S.T.M. continue to be the preferred methods of the laboratory running a large number of determinations since, under their conditions of operation, the man-hours per determination are lower by these methods. Other reasons for proposing modifications are the elimination of the Eschka mixture which is not easy to prepare in desirable physical form and may be expensive.

The early history of the development of methods for the determination of total

sulfur has been well reviewed by Strache and Lant.⁴⁰ The first really practical, reliable method was that of Eschka. Many modifications of the Eschka method have been proposed, but none have received any wide adoption.⁴¹ Stadnikoff and Titov⁴² recommended inverting the inner crucible containing the coal and Eschka mixture in a larger crucible and sealing the space between the two crucibles with Eschka mixture. Lanzmann⁴³ confirmed the accuracy of the Eschka method for high-sulfur coals and stated that the bomb-washing method gave variable results. Hackl,⁴⁴ however, proposed a mixture of equal parts of sodium carbonate and potassium permanganate in place of Eschka's mixture for high-sulfur coals. Otin and Cotrutz⁴⁵ checked Hackl's method against the Eschka method and found small differences between them, the variations being the greater with the Hackl method, which required longer heating. Ter Meulen⁴⁶ proposed heating the coal mixed with soda and magnesia in a porcelain boat in a quartz tube in a stream of air, passing the resultant gases over incandescent asbestos, absorbing any sulfur dioxide formed in potassium hydroxide solution, and adding that solution to the extract of the contents of the boat; he claimed that the results thus obtained were more nearly accurate. Ivison⁴⁷ found that calcium oxide did not give the same accuracy that magnesium oxide does. He stated that care must be exercised in selecting the calcium oxide used but that high purity is

not necessary. Thau and Wisser⁴⁸ have reviewed the Eschka, magnesium oxide, calcium oxide, and sodium peroxide methods and their improvements.

To cut down the time of ignition in the Eschka method, Lernerman⁴⁹ proposed igniting the coal with one-fifth of its weight of a mixture of 1 part of sodium carbonate and 2 parts manganese dioxide in a stream of pure oxygen, claiming that but 10 to 15 minutes was required by this procedure.

Bahr and Heide⁵⁰ proposed a rapid method in which the coal is heated with barium peroxide and an aluminum thermite. The sulfur forms barium sulfide, which is later decomposed with hydrochloric acid, the hydrogen sulfide being absorbed as cadmium sulfide and the sulfur determined iodometrically. The results by this method were higher than by the Eschka method even after blank correction. Melzer⁵¹ found this method to be inaccurate and proposed modifications.

Young⁵² proposed the use of a mixture of calcium oxide and sodium nitrate in place of Eschka mixture and found that the results were satisfactory for coals having less than 3 percent sulfur but were lower than results by the Eschka method for high-sulfur coals, for example, 0.18 percent for a coal containing 6 percent sulfur.

Sveshnikov and Smernova⁵³ stated that, if the ignition is carried out for a sufficiently long time (1.5 hours), there is no need to oxidize the solution with bromine

⁴⁸ Thau, A., and Wisser, W., *Wasser u. Gas*, **23**, 467-75 (1933).

⁴⁹ Lernerman, G. V., *J. Chem. Ind. (U.S.S.R.)*, **8**, 1087-9 (1931).

⁵⁰ Bahr, H., and von der Heide, W., *Z. angew. Chem.*, **37**, 848-51 (1924).

⁵¹ Melzer, W., *ibid.*, **38**, 976 (1925); *Brennstoff-Chem.*, **7**, 313-4 (1926).

⁵² Young, C. H., *Geol. Survey China, Reprint, Bull.* **23**, 5-12 (1933).

⁵³ Sveshnikov, A. T., and Smernova, E. V., *Zavodskaya Lab.*, **5**, 497-8 (1936); *Chem. Abs.*, **30**, 6165 (1936).

⁴⁰ See pp. 464-6 of ref. 10.

⁴¹ See pp. 37-42 of ref. 22.

⁴² Stadnikoff, G. L., and Titov, N. G., *Brennstoff-Chem.*, **13**, 285-7 (1932).

⁴³ Lanzmann, R., *ibid.*, **13**, 167 (1932).

⁴⁴ Hackl, O., *Chem.-Ztg.*, **52**, 933-4 (1928).

⁴⁵ Otin, C., and Cotrutz, G., *Brennstoff-Chem.*, **13**, 126-7 (1932).

⁴⁶ Ter Meulen, H., *Chem. Weekblad*, **24**, 206-7 (1927).

⁴⁷ Ivison, N. J., *Fuel*, **11**, 23-4 (1932).

water or hydrogen peroxide before precipitation of the barium sulfate.

Smith and Deem⁵⁴ tried perchloric acid as the digesting agent in the determination of sulfur in coal and coke but found the results erratic and low when compared with the Eschka method.

When the sulfur content of coal is determined by the bomb-washing method, the initial charge of air in the bomb should not be removed by flushing with oxygen since the oxides of nitrogen formed during the combustion act as catalysts in converting sulfur dioxide to sulfur trioxide.⁵⁵ Kohout⁵⁶ recommended adding from 10 to 15 percent of nitrogen to the oxygen in the bomb calorimeter, especially for high-sulfur coals, to facilitate the complete conversion of the sulfur to sulfur trioxide. The A.S.T.M. Method D271-37 states that filling the bomb with oxygen without displacing the original air should insure sufficient nitrogen for complete oxidation of the sulfur in the coal.

The peroxide method has been sponsored mainly by Parr,⁵⁷ particularly in connection with the turbidimetric method for estimating the barium sulfate, in order to make the method rapid. Methods have been proposed, especially in Russia, as being particularly rapid, in which the coal is burned in a stream of oxygen, the sulfur dioxide is picked up from the combustion gases in an oxidizing medium such as hydrogen peroxide or iodine water, and the resulting sulfuric acid is titrated. Certain

of these methods are also stated to be useful for simultaneously determining sulfur and ash. Vos'Kin⁵⁸ absorbed the sulfur dioxide in hydrogen peroxide and titrated the resulting sulfuric acid with 0.05 N NaOH. Kefeli and Berliner⁵⁹ titrated with 0.02 N sodium carbonate, and Khotenskii and Bogomolov⁶⁰ with hydrogen peroxide or sodium hypochlorite. Perederii⁶¹ moistened the coal with methyl alcohol to assist in the ignition and absorbed the sulfur dioxide in 3 percent hydrogen peroxide or iodine and titrated with sodium hydroxide. Fogelson, Kalmnikova, and Ponikaronskikh⁶² proposed the method of Kassler,⁶³ in which the sulfur dioxide is picked up in water and titrated as formed with iodine. A bit of starch is added to the water at the beginning of the test, a drop of the iodine solution is added, and then iodine is added as fast as the solution is decolorized. The titration is complete when the combustion is finished.

Many suggestions have also been made in reference to turbidimetric or volumetric methods for determining the sulfate resulting in any of the methods for determining coal sulfur. Application of the turbidimeter by Parr has already been mentioned. The turbidimeter has also been recommended by Tykac and Streit.⁶⁴ Pucherna⁶⁵ reported results too high by 6 percent using

⁵⁸ Vos'Kin, L. D., *Zavodskaya Lab.*, **3**, 614-6 (1934).

⁵⁹ Kefeli, M. M., and Berliner, E. R., *Coke and Chemistry (U.S.S.R.)*, **4**, No. 7, 62-5 (1934).

⁶⁰ Khotenskii, E. S., and Bogomolov, V. I., *Ukrain. Khim. Zhur.*, **8**, 386-92 (1933).

⁶¹ Perederii, M. P., *Coke and Chemistry (U.S.S.R.)*, **4**, No. 3, 64-5 (1934).

⁶² Fogelson, E. I., Kalmnikova, N. V., and Ponikaronskikh, M. I., *Zavodskaya Lab.*, **4**, 521-6 (1915).

⁶³ Kassler, I., *Chem.-Ztg.*, **57**, 573-4 (1933).

⁶⁴ Tykac, B., and Streit, J., *Paliva a Topeni*, **9**, 133-5 (1927).

⁶⁵ Pucherna, J., *Listy Cukrovar.*, **54**, 376 (1936).

⁵⁴ Smith, G. F., and Deem, A. G., *Ind. Eng. Chem., Anal. Ed.*, **4**, 227-9 (1932).

⁵⁵ Regester, S. H., *Ind. Eng. Chem.*, **6**, 812-22 (1914). Bradley, M. J., Corbin, R. M., and Floyd, T. W., *ibid.*, **18**, 583-4 (1926).

⁵⁶ Kohout, J. F., *ibid.*, **19**, 1065-6 (1927).

⁵⁷ Parr, S. W., *Univ. Illinois, Bull.*, **1**, No. 20 (1904), 40 pp.; *Illinois Univ. Studies*, **1**, 309-14 (1904); *J. Am. Chem. Soc.*, **22**, 646-52 (1900); *J. Ind. Eng. Chem.*, **11**, 230-1 (1919).

a photometer. Yurovski⁶⁶ used the Eschka method for obtaining the sulfate and placed the sulfate solution in a centrifuge tube of special design having a small cylindrical tip, then added barium chloride solution, heated to boiling, and centrifuged, reading the volume of barium sulfate by means of a specially calibrated steel scale.

Volumetric methods for determination of total sulfur have been suggested by several investigators.⁶⁷ Complete discussions of such methods will be omitted here since any valid method for the estimation of sulfate is suitable once the coal sulfur has been quantitatively transformed to sulfate.

SULFATE AND PYRITIC SULFUR

The methods for the determination of sulfate and pyritic sulfur which are in general use are those proposed by Powell and Parr,^{15, 35, 68}

The sulfate sulfur is determined by extracting the coal with 3 percent hydrochloric acid for 40 hours at 60° C, both the iron and sulfur content of the extract being determined. Pyritic sulfur is determined by extracting the coal with dilute nitric acid of 1.112 specific gravity for 2 to 3 days at room temperature. The nitric acid is evaporated, the residue from the evaporation is dissolved in hydrochloric acid, and the resulting solution is analyzed for iron and sulfur, the pyritic sulfur being the dif-

ference between the figure so obtained and the value for sulfate sulfur.

The methods of the United States Steel Corporation specify the addition of a few drops of bromine water from time to time during the digestion of the coal with nitric acid to assist in the solution and oxidation of the pyrite.⁶⁹ Yancey and Fraser⁸ boiled 5 grams of the coal with 50 cubic centimeters of 1.2 specific gravity hydrochloric acid for 1 hour, filtered, and determined the quantity of sulfur in the filtrate. They worked with coals which were low in sulfate, the highest value being 0.04 percent. According to von Walther and Bielenberg,⁷⁰ pure pyrite is not completely dissolved under such conditions, approximately 3 percent remaining undecomposed, but, for the low pyrite content of most coals, this error is insignificant.

Woolhouse,⁷¹ who studied these methods intensively, found that in general they were fairly accurate, but that it was always desirable to determine iron values together with the sulfur values so that some idea of the probable error involved might be obtained. The nature of the iron compounds dissolved in the hydrochloric acid varied from sample to sample and included ferrous compounds, hydrated ferric oxide, and ferric compounds. Mangubi and London,⁷² checking the methods of Powell and Parr, found that pyritic iron was satisfactory for the determination of pyrite. Young⁷³ claimed that dilute nitric acid extracted some organic sulfur and recommended the calculation of pyritic sulfur from quantities of extracted iron.

⁶⁹ See pp. 81-4 of ref. 37.

⁷⁰ Von Walther, R., and Bielenberg, W., *Braunkohlenarch.*, No. 17, 14-9 (1927).

⁷¹ Woolhouse, T. G., *Fuel*, 4, 454-6 (1925).

⁷² Mangubi, B. V., and London, M. E., *Coke and Chemistry (U.S.S.R.)*, 4, No. 4, 52-9 (1934).

⁷³ Young, C. H., *Fuel*, 15, 91-3 (1936).

⁶⁶ Yurovski, A. Z., *Coke and Chemistry (U.S.S.R.)*, 1933, No. 12, 75-6.

⁶⁷ Kobzareno, V. S., *Nauk. Zapiski Tzukrovoi Prom.*, 20, 39-42 (1932). Kefeli, M. M., and Berliner, E. R., *Zavodskaya Lab.*, 3, 201-4 (1934). Fogelson, E. I., and Kalmanikova, N. V., *ibid.*, 4, 342-4 (1935). Aronov, S. G., Moiseeva, K. M., and Treigermann, R. A., *Coke and Chemistry (U.S.S.R.)*, 4, No. 12, 51-4 (1935).

⁶⁸ Powell, A. R., and Parr, S. W., *Bull. Am. Inst. Mining Engrs.*, 1919, 2041-9; *Trans. Am. Inst. Mining Met. Engrs.*, 63, 674-82 (1920). Powell, A. R., *J. Ind. Eng. Chem.*, 12, 887-90 (1920); *U. S. Bur. Mines, Tech. Paper* 254 (1921), 21 pp.

London and associates⁷⁴ proposed a method in which 1 gram of the coal is ashed, the ash digested with hydrochloric acid, and the extracted iron determined by the Zimmermann-Reinhardt potassium permanganate method. Pyritic sulfur is calculated from the iron value so obtained minus the hydrochloric-acid-soluble iron in the original coal. Sulfate sulfur and hydrochloric-acid-soluble iron are determined in the extract obtained by digesting the coal with 10 percent hydrochloric acid brought to boiling. Pyritic sulfur can be obtained directly by the first method if the coal is thus treated with 10 percent hydrochloric acid before ashing.

Ranski and Chaikowa⁷⁵ described a method in which the coal is heated with tin and hydrochloric acid, and the hydrogen sulfide evolved is absorbed, determined, and calculated to pyritic sulfur.

The State Coal Survey Laboratory of the Fuel Research Board of Great Britain⁷⁶ has investigated the method of Powell and Parr, that of the United States Steel Corporation, that of London, Zhadanovskaya, Goncharenko, and Berger, and that of Ranski and Chaikowa for the determination of sulfate sulfur. They found that the United States Steel modification of the method of Powell and Parr gave a higher pyritic sulfur value than the original method and one which was more nearly in stoichiometric relationship to the pyritic iron. The addition of the bromine water did not lead to a materially different figure for pyritic iron. The method of London et al. gave a result in close agreement with that of the United States Steel Corpora-

tion method but is inaccurate if iron silicates are present. The method of Ranski and Chaikowa gave slightly higher values than the other methods and suffered from the long time required to carry it through. This laboratory also compared the methods of Powell and Parr, Yancey and Fraser, and London and associates for determining sulfate sulfur and found that, despite the shorter times of extraction in the Yancey and Fraser and London methods the results were in close agreement, at least for the sample studied.

ORGANIC SULFUR

Organic sulfur is usually considered to be the difference between the total sulfur and the sum of the sulfate and pyritic sulfur. Powell and Parr distinguished between phenol-soluble or resinic sulfur, and insoluble, or humic, organic sulfur, on the basis of the analyses of the phenol-soluble and phenol-insoluble material in the coal. Later references indicate that little or no use has been made of this method for subdividing organic sulfur.

COMBUSTIBLE SULFUR

More attention is given to the determination of the so-called combustible sulfur in Europe than in the United States. Combustible sulfur is considered to be that sulfur which passes off with the gaseous products of combustion when the coal is burned, the sulfur remaining in the ash being called ash sulfur, noncombustible sulfur, or fixed sulfur. Combustible sulfur is determined by burning the coal in an oxygen stream, absorbing the sulfur dioxide with bromic acid or hydrogen peroxide, and determining the sulfur as sulfate.⁷⁷ There

⁷⁴ London, M. E., Zhadanovskaya, A. P., Goncharenko, K. M., and Berger, E. B., *Coke and Chemistry (U.S.S.R.)*, **3**, No. 8, 45-51 (1933).

⁷⁵ Ranski, B. N., and Chaikowa, N. A., *Khim. Tverdogo Topliva*, **2**, No. 9, 73-6 (1933).

⁷⁶ Dept. Sci. Ind. Research (Brit.), *Fuel Research Rept. for the Year Ended March 31, 1937*, pp. 37-8.

⁷⁷ Saver, A., *Z. anal. Chem.*, **12**, 32-6 (1873). Holliger, M., *Z. angew. Chem.*, **22**, 436-49, 493-7 (1909). Lant, R., and Lant-Ekl, E., *Brennstoff-Chem.*, **2**, 330-2 (1921).

have been many variations of this procedure which are fully discussed in Strache and Lant⁷⁸ and in Muhlert.⁷⁹ It is apparent that several of the rapid methods for the determination of total sulfur by the oxidation of the coal in a stream of oxygen are actually methods for the determination of combustible sulfur if no account is taken of the sulfur which may remain in the combustion residue. For low-sulfur, low-ash coals, this may be negligible, but for high-ash, and especially for high-ash high-sulfur, coals there may be an appreciable difference.

The sulfur content of the ash may be determined by igniting the ash with sodium carbonate or Eschka mixture, extracting the ignited mixture with water, filtering, completing the oxidation with bromine water or hydrogen peroxide, and precipitating the sulfur as barium sulfate.^{36, 37, 78} Thieler⁷⁹ recommended spreading the ash in a thin layer on a layer of potash in a platinum crucible, covering the ash with a mixture of potassium carbonate and potassium nitrate, and igniting in an electric muffle until all solid particles dissolved. The crucible contents were extracted with water and the sulfate determined gravimetrically.

SULFIDE SULFUR

Sulfides are not found in coal but are in coke. Sulfide sulfur occurs mainly as iron sulfide but may also be present as calcium sulfide. It is determined by evolution methods in which the hydrogen sulfide is released from the sulfides in the coke as hydrogen sulfide, absorbed as cadmium sulfide, and determined, usually volumetrically.⁸⁰

⁷⁸ See pp. 466-70 of ref. 10 and pp. 42-4 of ref. 22.

⁷⁹ Thieler, E., dissertation, Aachen, 1912.

⁸⁰ See pp. 84-6 of ref. 37.

THE SULFUR CONTENT OF COALS

The determination of the total sulfur content of coal is part of both the proximate and the ultimate analysis of coal.⁸¹ Proximate and ultimate analyses of coal, therefore, almost always include values for sulfur. Because of the variability of the sulfur content of coals from place to place and from seam to seam and even within the seam itself over small areas, publication of individual values here would serve no useful purpose. Compendia of analyses of coals published by federal, state, business, and trade organizations regularly carry values for the total sulfur content of the coals whose analyses they report. One of the earliest collections of analyses of United States coals which includes sulfur determinations, and which is largely of historical interest, is that by Johnson.⁸²

Determinations of the amounts of pyritic, sulfate, and organic sulfur have in the past been less frequently carried out, but the more recent tendency has been to include these determinations on samples of coal collected at the face or tippie in connection with surveys of mineral resources and for samples in connection with studies of coal cleaning and carbonization. This is especially true for the higher-sulfur coals. The pyritic, sulfate, and organic sulfur contents of those coals being studied in the U. S. Bureau of Mines-American Gas Association Survey of the Coal, Coke, and Gas-Making Properties of American Coals are usually determined.⁸³

Analyses of Canadian coals are contained

⁸¹ Haslam, R. T., and Russell, R. P., *Fuels and Their Combustion*, McGraw-Hill Book Co., New York, 1926, p. 24.

⁸² Johnson, W. R., *A Report to the Navy Department of the United States on American Coals Applicable to Steam Navigation and to Other Purposes*, 29th Congress, 1st Session, Document 386, 1844, 600 pp.

⁸³ Wilson, J. E., and Davis, J. D., *U. S. Bur. Mines, Tech. Paper 637* (1942), 10 pp.

in the reports of the Canadian Division of Fuels and Fuel Testing, Mines Branch, Canada Department of Mines; those of British coals are contained in the reports of the Physical and Chemical Survey of the National Coal Resources of the Department of Scientific and Industrial Research of Great Britain.

Von Bitto⁸⁴ reported the total sulfur, "combustible sulfur," and noncombustible sulfur contents of fifty Hungarian coals.

THE INFLUENCE OF PYRITES ON THE SPONTANEOUS COMBUSTION OF COAL

The spontaneous ignition of coal has often been attributed to the presence of pyrite. That pyrite is solely responsible for the spontaneous ignition of coal has been rather definitely disproved. On the other hand, there are at least certain conditions under which the presence of pyrite definitely increases the susceptibility of stored coal to spontaneous ignition. The early literature on the influence of pyrites on the spontaneous combustion of coal has been reviewed by Parr and Kressman⁸⁵ and by Davis and Byrne.⁸⁶ The relation of pyritic oxidation to the spontaneous combustion of coal has also been studied by Macpherson, Simpkin, and Wild,⁸⁷ who stated that their results emphasize the importance that must be attached to the mode of existence in the pyrite when considering its probable influence on the spontaneous combustion of coal. Parr and Kressman⁸⁵ concluded that the presence of sulfur in the form of iron pyrite is a positive source of heat due to the reaction between sulfur and

oxygen. Davis and Byrne⁸⁸ concluded that "Artificial mixtures of coal and pyrite in various proportions showed a critical temperature no lower than that of the coal alone, while pure pyrites had a critical temperature 26° C higher than the coal. From this it appears that massive pyrite or 'brass lumps' are not dangerous in a coal pile. Iron sulfide finely disseminated in microscopic nodules may be a subsidiary cause of heating, but to just what extent is not known. The distinction between the action of pyrite and marcasite has not been definitely established, nor have the microscopic nodules been identified absolutely as marcasite or pyrite. This point would merit further investigation." The British Departmental Committee of the Home Office on Spontaneous Combustion of Coal in Mines concluded from the evidence presented to them that "some small amount of heat may be developed by the oxidation of pyrites in coal when it occurs as an amorphous form of marcasite; but that, as pyrites is present in coal in such small proportions as compared with the coal substance proper—which is a bad conductor of heat—the effect of this heat is negligible. The chief part played by pyrites when present in an unstable form is that of a disintegrator of the coal, so rendering the latter more permeable by air and exposing a greater area of coal substance to oxidation."⁸⁹

Francis and Wheeler⁹⁰ stated, "It is now recognized that, whilst on occasion the presence of pyrites may be a contributing or even a determining factor, the main cause of the spontaneous combustion of

⁸⁴ Von Bitto, B., *Z. angew. Chem.*, **8**, 37-41 (1895).

⁸⁵ Parr, S. W., and Kressman, F. W., *Univ. Illinois, Eng. Expt. Sta., Bull.* **46**, 57-82 (1910).

⁸⁶ Davis, J. D., and Byrne, J. F., *Carnegie Inst. Tech., Coop. Bull.* **3**, 21-3 (1922).

⁸⁷ See p. 15 of ref. 19.

⁸⁸ See pp. 35-6 of ref. 86.

⁸⁹ *Brit. Mines Dept., Com. of the Home Office on Spontaneous Combustion of Coal in Mines*, H. M. Stationery Office, *Cmd. 1417* (1921), 114 pp.

⁹⁰ Francis, W., and Wheeler, R. V., *Safety in Mines Research Board (London), Paper 28*, **3** (1926).

coal is the direct action of the oxygen of the air on the coal substance. The study of the spontaneous combustion of coal has, therefore, resolved itself into a study of the character of the reactions between oxygen and the coal substance at low temperatures."

The greatest influence of pyrites on the spontaneous ignition of stored coal is probably its action in breaking up the coal upon oxidation. In moist air or in moist aerated conditions pyrite oxidizes to ferrous sulfate, which is greater in volume than the original pyrite. The formation of ferrous sulfate causes the coal to crack and crumble away and increase in surface area. Any tendency toward heating is thereby aggravated.

Pyrite recovered from coal for commercial shipment has been known to ignite spontaneously while stored in railway cars. This is a hazard which must be guarded against.

THE UTILIZATION OF COAL SULFUR

In a year of good activity, 500,000,000 tons of coal are mined in the United States. Assuming that coal will average 1 percent of sulfur, this coal will carry 5,000,000 tons of sulfur or from 2 to 2.5 times the average annual consumption of sulfur by the entire United States industry in the decade from 1930 to 1940. The major proportion of this sulfur eventually finds its way to the atmosphere as sulfur dioxide. The idea of recovering this sulfur has at times intrigued many people, both from the standpoint of eliminating its nuisance in the atmosphere and from the standpoint of adding to the mineral resources of the country.

The commercial recovery and utilization of coal sulfur would be profitable or practical only under certain special conditions. Sulfur may be recovered as pyrite during mining and preparation of coal, as sulfur

or sulfur compounds in the manufacture of coal gas, producer gas, water gas, and the like, or by scrubbing the gaseous products of combustion of coal. Spetl⁹¹ has reviewed the whole field of possible utilization of coal sulfur.

When pyrite occurs in massive bands or lenses it can frequently be recovered in commercially acceptable form at relatively low cost. This recovery may start at the mine face with the segregation of lenses and massive bands and continue through to the tippie or cleaning plant with the segregation and purification of highly pyritic refuse. A threatened shortage of sulfur for sulfuric acid manufacture in the United States during the first World War awakened interest in the possibilities of recovering suitable pyrite in connection with coal-mining operations. The U. S. Bureau of Mines and various state geological surveys estimated the potentially available supplies and proposed procedures and plant. Before any great progress was made, the end of the war and the rapid development of the native sulfur deposits in Louisiana and Texas by the Frasch process made economic conditions again unfavorable for coal pyrite recovery. Yancey⁹² reported on the nature of pyrite samples collected by the U. S. Bureau of Mines in cooperation with various state geological surveys—Ohio, Missouri, Indiana, Tennessee, Kansas, Kentucky, Illinois, Pennsylvania, and Michigan. Most of these samples contained over 40 and practically all contained more than 35 percent sulfur. This survey, according to Holbrook,⁹³ showed that a total of 1,456,000 tons of pyrite containing more than 40 percent sulfur were available per year at that

⁹¹ Spetl, F., *Chem. Obzor*, **11**, 115-7 (1938).

⁹² Yancey, H. F., *Chem. & Met. Eng.*, **22**, 105-9 (1920).

⁹³ Holbrook, E. A., *Trans. Am. Inst. Mining Met. Engrs.*, **63**, 638-40 (1920).

time from those mines only whose coals would yield more than 1 percent of sulfur. The estimates for the individual states were as follows:

	TONS PER YEAR
Kansas	125,000
Missouri	175,000
Iowa	140,000
Illinois	238,000
Indiana	250,000
Kentucky	25,000
Tennessee	56,000
Michigan	12,000
Ohio	235,000
Pennsylvania	200,000

A survey had previously been made by the State of West Virginia, but figures were not available.

An objection to the use of coal pyrite for the manufacture of sulfuric acid was its associated carbon content, the carbon dioxide resulting from its combustion being said to decrease the efficiency of the chamber process and tarry matter which sometimes escaped through the burners darkening the acid. Yancey stated that the harmful influence of carbon dioxide on the chamber process was due to incomplete understanding of the proper conditions and that successful acid production could be attained without trouble, using pyrites containing up to 10 percent carbon, though he recommended that the maximum should be 8 percent carbon. Parrish⁹⁴ recommended that pyrite for sulfuric acid manufacture should have a minimum sulfur content of 38 percent and a maximum ferrous sulfate content of 6 percent.

Hart⁹⁵ reported that Messrs. Chance at Gidbury, England, had manufactured sulfuric acid from coal pyrite, the acid being dark from the carbonaceous matter con-

taminating the pyrites. The acid was acceptable to its purchasers, so much so that they objected to light-colored acid later produced from pure pyrite, and this acid had to be colored by the addition of charred sugar to satisfy them. The Consolidated Coal Company was reported by Holbrook to have erected a sulfuric acid plant at Fairmont, W. Va., to use pyrite recovered from coal.

Compared to commercial pyrite, coal pyrite is low in arsenic. Arsenic contents in percentages of coal pyrite samples from various states in the United States have been reported by Yancey⁹² as follows: Pennsylvania, 0.056, 0.039; Illinois, 0.029, 0.005; Ohio, 0.005; and Tennessee, 0.015. Phosphorus contents also were low, ranging from 0.003 to 0.035 percent, seven samples having less than 0.015 percent phosphorus and four samples less than 0.008 percent. Holbrook²⁹ reported that pyrite from Illinois coal contained no arsenic or antimony.

Holbrook²⁹ has reviewed the recovery of pyrite in Illinois up to 1917 and has reported studies on possible methods and equipment for the commercial recovery of pyrite for acid making. Smith and Mitchell⁹⁶ stated that pyrite for the manufacture of sulfuric acid was being recovered at two plants in Illinois in 1936.

Holbrook and Nelson²⁹ using the ore-dressing pilot plant at the University of Illinois also investigated the possibility of obtaining marketable pyrite concentrates from Tennessee coal. They estimated that at that time plants to produce 50 and 100 tons of pyrite concentrate per 8 hours would cost \$14,000 and \$20,000 respectively.

Parsons, Anderson, Johnston, and Jen-

⁹⁴ Parrish, P., *Gas J.*, **141**, 246-7 (1918).

⁹⁵ Hart, E., *Trans. Am. Inst. Mining Met. Engrs.*, **63**, 638 (1920).

⁹⁶ Smith, C. M., and Mitchell, D. R., *Univ. Illinois, Eng. Expt. Sta., Bull.* **235** (1936), 44 pp.

kins⁹⁷ described the procedure used at the Dominion Coal Company, Sydney, Nova Scotia. Washery waste containing 11 percent sulfur was ground in a closed circuit with a Dorr classifier. The overflow was passed over a 48 by 65 mesh screen to take out coarse clean coal, and the fines were floated to give a clean concentrate. The tailings contained most of the sulfur, which were thickened to 35 percent solids content and floated to recover pyrite. Faddeen⁹⁸ reported on various methods of concentrating coal pyrite and stated that the results were generally unsatisfactory. Yancey and Taylor,⁹⁹ studying the froth flotation of coal for purposes of sulfur and ash reduction, found that the oxidation products of pyrite are powerful pyrite depressants and suggested the use of iron salts as depressants for pyrite. More recent work further substantiates the conclusions of the earlier work that there are no serious technical difficulties in the way of pyrite recovery in the course of coal mining, but that in normal times the economic feasibility is questionable.¹⁰⁰

Since quality requirements for pyrite for sulfuric acid manufacture are fairly high, attempts have been made to find other uses for coal pyrite. Postmkor, Kuz'min, and Krillov¹⁰¹ have given a method for recovering free sulfur from pyrite contaminated with carbon. The pyrite is

mixed with 10 to 15 percent of coal and heated to 600 to 800° C in a stream of gas deficient in oxygen. Free sulfur is formed in yields of 80 percent. The layer of pyrite should be thick and the stream of gas rapid. At first hydrogen sulfide is formed through the action of the water present in the coal. Later, sulfur dioxide forms when the carbon is used up. Muhlert¹⁰² suggested that a use for coal pyrite is its conversion at a coke-oven plant into sulfur dioxide which may be used to react with the hydrogen sulfide in the gas to form elemental sulfur, or in the recovery of ammonium sulfate, or in some modification of the Feld polythionate process. The gas obtained during the carbonization of coal contains a part of the sulfur originally present in the coal. As has been mentioned elsewhere, the proportion of the total sulfur which will be found in gas depends upon the distribution of the sulfur varieties in the coal and the conditions of carbonization. For most purposes, and especially when the gas is sold for domestic consumption, the sulfur in the gas is highly undesirable and must be removed. Attempts have naturally been made to recover it from the gas in useful form.

As will be described in more detail in another section of this book (see Chapter 26), sulfur compounds may be removed from the gas by dry or by wet purification processes. The main dry purification processes involve the absorption of the hydrogen sulfide by means of iron oxide or the absorption of the sulfur compounds by means of activated carbon or other active absorbing agents. The wet purification processes either absorb the hydrogen sulfide or convert it into other compounds.

In the dry purification of coal gas by means of iron oxide, the sulfur present in

⁹⁷ Parsons, C. S., Anderson, A. K., Johnston, J. D., and Jenkins, W. S., *Can. Dept. Mines, Mines Branch, Rept. 736* (1934), pp. 32-4.

⁹⁸ Faddeen, I. V., *Gorno-Obogatitel. Delo*, **1929**, No. 2, 49-80.

⁹⁹ Yancey, H. F., and Taylor, J. A., *U. S. Bur. Mines, Rept. Investigations 3263* (1935), 20 pp.

¹⁰⁰ Bixby, K. R., *Min. Congr. J.*, **23**, No. 11, 16-20 (1937); *Colliery Guardian*, **155**, 1223-5 (1937). Döring, A., and Erberich, G., *Glückauf*, **74**, 537-40 (1938). Köhlwein, F. L., and Lohman, G., *ibid.*, **74**, 540-6 (1938).

¹⁰¹ Postmkor, V. V., Kuz'min, L. L., and Krillov, I. P., *Angew. Chem.*, **47**, 668-71 (1934); *J. Chem. Ind. (U.S.S.R.)*, **1934**, No. 6, 22-6.

¹⁰² Muhlert, F., *Chem. Fabrik*, **9**, 273-81 (1936).

the gas as hydrogen sulfide is absorbed and eventually converted during the reactivation of the oxide into free sulfur. Spent oxide may contain from 30 to 50 percent free sulfur, depending upon the conditions of operation. In American practice, spent oxide usually contains about 30 percent sulfur; in European, the sulfur is frequently allowed to build up to 50 percent.¹⁰³

This sulfur may be recovered by extraction of the spent oxide with solvents for sulfur with subsequent recovery of the solvent for reuse. Carbon bisulfide has been found to be most satisfactory for this purpose. Benzol, tetralin, and high-boiling solvent naphtha have not proved satisfactory. Although carbon bisulfide is used on a large scale in other industries, it has not found extensive application in the coke industry because of the hazards it involves. The solvents also dissolve tar and hydrocarbons that contaminate the sulfur. Processes for the purification of the sulfur solution have been proposed in which the solution is filtered through clarifying clays or treated with a mixture of sulfur and nitric acids or a chlorosulfonic acid.¹⁰⁴

In another process¹⁰⁵ the sulfur is extracted by means of an ammonium polysulfide solution which is later boiled to precipitate the dissolved sulfur. Processes for the extraction of sulfur are not generally profitable unless the operations can be conducted on a very large scale. The Ruhrgas A.-G. constructed a central plant at Horst-Gelsenkirchen for the treatment of spent oxide obtained from surrounding gas plants. This plant had a capacity of treating 16,000 to 17,000 tons of spent

oxide, containing 7,000 tons of sulfur and representing 1,000,000,000 cubic meters of gas out of the total of 4,500,000,000 cubic meters of gas produced in Germany. It was estimated that the equivalent of 27,000 tons of sulfur could be obtained in this manner from the total 4,500,000,000 cubic meters of gas. The cost of dry purification of gas containing 6 grams of hydrogen sulfide per cubic meter at the Hamborn, Germany, Gas Works, including the cost of extracting the sulfur, was 43.78 pfennigs per 1,000 cubic meters. Allowing for the value of the sulfur and ferrocyanide recovered, this cost became 39 pfennigs. In contrast, the purification of a similar gas by the Thylox process cost 19 pfennigs.¹⁰² The spent oxide may also be burned and the sulfur dioxide so obtained converted to sulfuric acid for use, for example, in recovering ammonia as ammonium sulfate.¹⁰⁶

In the wet purification processes, the hydrogen sulfide may be absorbed and recovered as such as in the Koppers phenolate and hot actification carbonate purification systems and subsequently used, for example, in the manufacture of sulfuric acid, or the hydrogen sulfide may be made to react to give free sulfur, sulfates, thio-sulfates, or some other sulfur-containing compound. Although the reactions of sulfur are complex and allow of many possibilities, apparently few, if any, have been overlooked by investigators in this field. (See Chapter 26.)

Among the earliest of the liquid purification processes was that of Claus,¹⁰⁷ in which the gas was scrubbed with ammonia liquor, the resulting liquors being distilled under columns and hydrogen sulfide and carbon dioxide being liberated while

¹⁰³ Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coke Industry*, Chemical Catalog Co., New York, 1932, p. 537.

¹⁰⁴ I. G. Farbenindustrie A.-G., Ger. Pat. 428,087 (1926).

¹⁰⁵ I. G. Farbenindustrie A.-G., Ger. Pat. 428,983 (1926).

¹⁰⁶ Wagner, F. H., *Coal Gas Residuals*, McGraw-Hill Book Co., New York, 1918, p. 191.

¹⁰⁷ Claus, C. F., Ger. Pats. 23,763 (1883), 39,277 (1886); *J. Gasbeleucht.*, 30, 1140 (1887). Joly, H., *ibid.*, 30, 1033-8 (1887).

the ammonia remained in solution. The liberated gases were burned in a special column and elementary sulfur was recovered. The difficulties encountered here are due to the fact that the carbon dioxide content is frequently several times the hydrogen sulfide content and the combustion of hydrogen sulfide is thereby prevented. Similar processes have been suggested by others.¹⁰⁸

Hydrogen sulfide and sulfurous acid react to form elemental sulfur. This is a fundamental reaction on which a number of processes are based. Estcourt, Veevers, and Schwab¹⁰⁹ proposed the use of calcium chloride solution, regenerating the spent solution by treatment with sulfurous acid to convert the absorbed hydrogen sulfide to sulfur. Behrens¹¹⁰ patented the process of washing the gas with a solution of sulfurous acid and converting the thionic acids formed into sulfur and sulfurous acid by evaporation. To accelerate the reaction between the hydrogen sulfide and the sulfurous acid the solution may be dispersed as a fine mist.¹¹¹

Hydrogen sulfide in solution treated with ammonium sulfite is converted into sulfur¹¹² or on heating into sulfate and sulfur.¹¹³ The gas when treated with sulfurous acid at high temperature may convert the hydrogen sulfide directly into sulfate and sulfur.¹¹⁴ The reaction may be accelerated by catalysts, for example, aluminum

sulfite.¹¹⁵ By washing the gas with a solution of sodium sulfite or bisulfite, sodium thiosulfate can be formed directly.¹¹⁶ Processes have been developed using ammonium sulfite and bisulfite in which conditions are held so as to show a minimum tension of hydrogen sulfide and sulfur dioxide.¹¹⁷ According to Terres and Hahn,¹¹⁸ this condition is met by a solution of sulfite and bisulfite in which there are about 1.3 to 1.6 molecules of ammonia for each molecule of sulfur dioxide. The process was worked for some time in a small experimental plant with a daily throughput of 176,000 cubic feet,¹¹⁹ at the Auguste Viktoria Colliery Company, but it has not been possible to introduce it on a large scale, evidently because the reactions are too complicated and also because it is not sufficiently flexible with regard to the products made.¹²⁰

Feld¹²¹ attempted to recover the sulfur present in the hydrogen sulfide and the ammonia in the gas as ammonium sulfate by means of his polythionate process.¹²²

H. Koppers A.-G. has proposed a modification of this system known as the C.A.S. system. Other processes attempting to recover the sulfur as ammonium sulfate are those of Burkheiser.¹²³ In spite of the

¹¹⁵ Fritsche, P., Ger. Pat. 250,243 (1910), 251,353 (1911).

¹¹⁶ I. G. Farbenindustrie A.-G., Ger. Pat. 431,307 (1926).

¹¹⁷ Hansen, C., Ger. Pats. 504,640, 523,678, 524,792, 526,079, 527,220 (1926).

¹¹⁸ Terres, E., and Hahn, E., *Gas- u. Wasserfach*, **70**, 389-95 (1917).

¹¹⁹ Overdick, F., *Z. angew. Chem.*, **43**, 1048-51 (1930).

¹²⁰ See p. 551 of ref. 103.

¹²¹ Feld, W., *Z. angew. Chem.*, **25**, 705-11 (1912).

¹²² Raschig, F., *Z. angew. Chem.*, **33**, 260-2 (1920). Funcke, W., *Glückauf*, **60**, 835-40, 868-76, 897-905 (1924).

¹²³ Burkheiser, W., Ger. Pats. 212,209 (1907), 215,907, 217,315 (1908), 223,713 (1909); *Gas- u. Wasserfach*, **69**, 765-71 (1926). Terres, E.,

¹⁰⁸ Hills, F. C., Brit. Pat. 1,369 (1868). O'Neill, J. C., *Proc. Am. Gas Inst.*, **1**, 461-70 (1913). Krieger, A., Ger. Pat. 322,938 (1920). H. Koppers A.-G. and Hansen, C., Ger. Pat. 504,777 (1928).

¹⁰⁹ Estcourt, C., Veevers, H., and Schwab, M., Ger. Pat. 45,948 (1887).

¹¹⁰ Behrens, J., Ger. Pat. 300,036 (1919).

¹¹¹ Allgemeine Vergasungs-G.m.b.H., Ger. Pat. 309,159 (1919).

¹¹² Bergfeld, L., Ger. Pat. 290,509 (1912).

¹¹³ Generator A.-G., Ger. Pat. 310,124 (1919).

¹¹⁴ Aktiengesellschaft Produkte-Fabrik Pommersdorf, Ger. Pat. 300,383 (1917).

many processes which have been proposed for recovering sulfur in one form or another, those which have achieved commercial success in America are the Koppers phenolate process for the recovery of the hydrogen sulfide in useful form as such and the Thylox, Ferroxy, and Nickel processes of the Koppers Company,¹²⁴ which recover elemental sulfur. Of these the Thylox process is most widely used and produces a sulfur of extremely fine particle size which has found extensive application either in paste, dust, or dry wettable form as an agricultural spray material.¹²⁵ The Thylox sulfur may be converted to brimstone by treatment in an autoclave; the sulfur and the gas may also be used in certain processes for producing ammonium thiocyanate.¹²⁶

When coal is burned most of the sulfur it contains escapes to the atmosphere as sulfur dioxide,¹²⁷ the obnoxious effects of which have long been recognized. Attempts to decrease this nuisance by decreasing the sulfur content of the coal can be only partly successful, since it is both physically and economically impossible to remove all the sulfur in the coal. If pollution of the atmosphere by sulfur dioxide from coal combustion is to be eliminated, the flue gas must be treated. Sulfur dioxide removal from the flue gases from large power plants in the London area is now required by law and entails large investments and operating costs. Wider enactment of such laws is hindered by the fact that economi-

cal means for complying with them are not available.

Recovery of the sulfur present in the flue gas in commercially valuable form provides a solution to the problem of disposing of the extracted sulfur compounds; moreover, the sale of these compounds will at least partly compensate for the cost of their removal. Attempts have been made to recover this sulfur as sulfuric acid, sulfur dioxide, and sulfite or sulfate salts. Johnstone and his coworkers in the United States have actively investigated this entire field and have reported their work on the production of dilute sulfuric acid by the catalytic oxidation of sulfur dioxide in solution¹²⁸ and on the absorption and regeneration of sulfur dioxide by ammonia solution,¹²⁹ by other solvents,¹³⁰ and by the use of zinc oxide.¹³¹

Reports also have been published on the design of absorption towers for treating large quantities of gases¹³² and on the economics of sulfur removal.¹³³ In the zinc oxide process, the gases are scrubbed with an alkaline solution, the solution is clarified to remove ash solids, and the absorbing solution is treated with zinc oxide, whereby

¹²⁸ Johnstone, H. F., *Ind. Eng. Chem.*, **23**, 559-62 (1931); *Proc. 3rd Intern. Conf. Bituminous Coal*, **1931**, 576-92; *Combustion*, **5**, No. 2, 19-30 (1933); *Univ. Illinois, Eng. Expt. Sta., Reprint 2* (1933), 32 pp. Johnstone, H. F., and Leppla, P. W., *J. Am. Chem. Soc.*, **56**, 2233-S (1934).

¹²⁹ Johnstone, H. F., *Ind. Eng. Chem.*, **27**, 587-93 (1935), **29**, 1396-S (1937). Johnstone, H. F., and Keyes, D. B., *ibid.*, **27**, 659-65 (1935). Johnstone, H. F., Read, H. J., and Blankmeyer, H. C., *ibid.*, **30**, 101-9 (1938).

¹³⁰ Johnstone, H. F., and Kleinschmidt, R. V., *Trans. Am. Inst. Chem. Engrs.*, **34**, 181-98 (1938).

¹³¹ Johnstone, H. F., and Singh, A. D., *Univ. Illinois, Eng. Expt. Sta., Bull.* **324** (1940), 140 pp.

¹³² Johnstone, H. F., and Singh, A. D., *Ind. Eng. Chem.*, **29**, 286-97 (1937).

¹³³ Johnstone, H. F., *Power Plant Eng.*, **42**, 538-9 (1938).

and Hahn, E., *ibid.*, **70**, 309-12, 339-43, 363-7, 389-95 (1927). Also see pp. 551-5 of ref. 103.

¹²⁴ See pp. 563-78 of ref. 103.

¹²⁵ Jacobson, D. L., *Chem. Markets*, **29**, 363 (1931). Sauchelli, V., *Ind. Eng. Chem.*, **25**, 363-7 (1933).

¹²⁶ See pp. 515-21 of ref. 103.

¹²⁷ Burdick, L. R., and Barkley, J. F., *U. S. Bur. Mines, Information Circ.* **7065** (1939), 23 pp.

the sulfur dioxide is converted to insoluble zinc sulfite. The zinc sulfite is filtered from the absorbing solution; the solvent is returned to the scrubber; and the zinc sulfite is dried and calcined to yield sulfur dioxide, water vapor, and zinc oxide.

Imperial Chemical Industries, Ltd., has developed a process for the removal of sulfur dioxide from flue gases by scrubbing them with lime slurry.¹³⁴ This process is in use at the Fulham Station in London and at the Tir John Station in Swansea, Wales. The development of this process, the success of which depends upon the circulation of large quantities of a slurry of calcium sulfite and calcium sulfate crystals to prevent crystallization on the scrubber surfaces, has been described by Lessing.¹³⁵ The cost of carrying out the process is stated to be 58 cents per ton of 1.5 percent sulfur coal, of which 21 cents is for lime.

Two cyclic processes developed in Europe for the recovery of sulfur dioxide from smelter gases, one using basic aluminum sulfate¹³⁶ and the other a xyldine-water mixture,¹³⁷ have been found to be unsuited for use with flue gases.¹³⁸

THE BEHAVIOR OF VARIETIES OF SULFUR ON CARBONIZATION

When coal is carbonized a portion of the sulfur in the coal is found in the gaseous products, another portion in the liquid products, and the remainder in the coke; the distribution among these products is of great commercial importance.

That the distribution of coal sulfur among the products of coal carbonization is at least of equal importance to the total

sulfur content of coals to be used for gas or coke manufacture is indicated by the fact that the maximum sulfur contents permitted in the A.S.T.M. specifications¹³⁹ for these coals are not stated directly but in terms of maximum sulfur contents of the coke and gas made from them. These specifications are as follows for gas coals:

The composition of gas coal shall be such that the dry coke produced therefrom will contain not over 1.5 percent of sulfur and the resultant gas will contain not more than 30 grains of sulfur, in the form of compounds other than hydrogen sulfide, per 100 cubic feet of gas.

For coking coals:

If metallurgical coke is to be produced, the composition of the coking coal shall be such that the dry coke produced therefrom will not contain more than 1.0 percent of sulfur in the case of foundry coke and 1.3 percent of sulfur in the case of blast-furnace coke. If gas is to be sold for domestic use, the composition of the coking coal shall be such that the resultant gas will contain not more than 30 grains of sulfur in the form of compounds other than hydrogen sulfide per 100 cubic feet of gas.

Early investigators considered only the total sulfur in this connection. More recent studies have almost always considered this problem from the standpoint of the behavior of the individual forms in which the sulfur is present in coal.

Holgate¹⁴⁰ carbonized 22.4-pound charges of coal in a small D-shaped gas retort and determined the sulfur contents of the coal, coke, gas, and tar in terms of the original coal and also the combustible sulfur in the coke and the sulfur remaining in the ash. The results varied widely even for coals from the same bed. The sulfur

¹³⁴ Pearson, J. L., Nonhebel, C. C., and Ulander, P. H. N., *J. Inst. Fuel*, **8**, 119-56 (1935).

¹³⁵ Lessing, R., *J. Soc. Chem. Ind.*, **57**, 373-88 (1938).

¹³⁶ Applebey, M. P., *ibid.*, **56**, 139-46T (1937).

¹³⁷ Roesner, G., *Metall u. Erz*, **34**, 5-11 (1937).

¹³⁸ See ref. 129.

¹³⁹ Am. Soc. Testing Materials Designation D166-24, *Am. Soc. Testing Materials Standards*, 1939, Pt. III, pp. 9-10.

¹⁴⁰ Holgate, T., *J. Gas Lighting*, **57**, 1124-5 (1891).

passed into the volatile materials amounted to 15.63 to 81.60 percent with a mean of 39.23 percent for the coals, mainly Yorkshire coals, and from 11.98 to 77.46 percent with a mean of 31.49 percent for eleven cannel coals.

Parr¹⁴¹ has presented values for volatile, fixed, and total sulfur for 150 Illinois coals. His results showed that, under the conditions of the laboratory volatile-matter test which he used, 51.5 percent of the total sulfur in the coal was discharged in the

sulfur content remaining practically constant. The ratio of pyritic sulfur to total sulfur ranged from 0.1477 to 0.6214. On carbonization the ratio of sulfur in the coke as calculated back to the original coal basis to the sulfur content of the original coal ranged from 0.477 to 0.581. Campbell¹⁴⁵ stated that most of the coal sulfur was present as pyrite and that 42 percent of this was volatilized during carbonization, the remainder (58 percent) existing in the coke as pyrrhotite. Powell¹⁴⁶ studied the

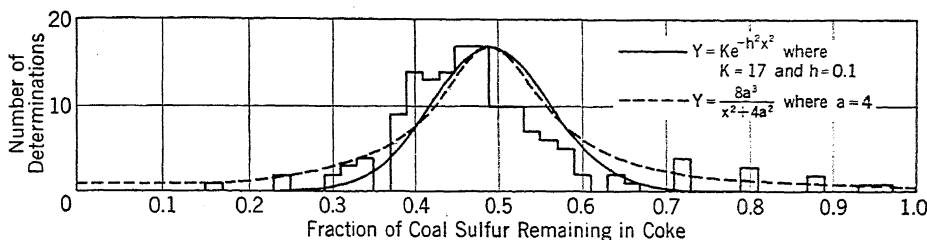


FIG. 1. Frequency distribution of the fraction of coal sulfur remaining in coke.¹⁴²

volatile matter. The ratios of fixed to volatile sulfur calculated from Parr's original data ranged from 0.16 to 0.96, the majority of the ratios falling in the range 0.378 to 0.592 and averaging 0.485. The frequency distribution of the values, plotted by Thiessen,¹⁴² is shown in Fig. 1.

Fulton¹⁴³ ascribed the variations in the proportions of the sulfur expelled from different coals as due to the different relative percentages of the sulfur forms present.

McCallum¹⁴⁴ separated a coal into different fractions by specific-gravity methods, and thereby secured samples of the same coal having increasing ratios of pyritic to organic sulfur with the organic

behavior of the different forms of coal sulfur during carbonization. He concluded that pyrite and marcasite decomposed to ferrous sulfide, pyrrhotite, and hydrogen sulfide, the reaction beginning at 300° C, reaching a maximum between 400 and 500° C, and being complete at 600° C; that sulfates were reduced to sulfides, the reaction being complete at 500° C; that part of the organic sulfur is volatilized as hydrogen sulfide, one-fourth to one-third, at most one-half, of the organic sulfur reacting this way; that part of the organic sulfur formed volatile organic sulfur compounds, especially during the lower temperatures of the coking process; that part of the organic sulfur formed complexes with carbon between 400 and 500° C which show none of the properties of the original coal sulfur;

¹⁴¹ Parr, S. W., *Univ. Illinois, Bull.* **1**, No. 20 (1904), 40 pp.

¹⁴² Thiessen, G., *Ind. Eng. Chem.*, **27**, 473-8 (1935).

¹⁴³ Fulton, J., *Treatise on Coke*, International Textbook Co., Scranton, Pa., 1905, pp. 38-40.

¹⁴⁴ McCallum, A. L., *Chem. Engr.*, **11**, 27-8 (1910); *Can. Mining J.*, **30**, 531-2 (1909).

¹⁴⁵ Campbell, J. R., *Trans. Am. Inst. Mining Engrs.*, **54**, 181-4 (1916).

¹⁴⁶ Powell, A. R., *J. Ind. Eng. Chem.*, **12**, 1069-77 (1920), **13**, 33-5 (1921).

and that, finally, a portion of the ferrous sulfide formed from the pyrite reacts with carbon. Sperr¹⁴⁷ stated that high-temperature cokes from coals containing from 0.5 to 3 percent sulfur have sulfur contents that average about 80 percent of the sulfur content of the coal. These values for sulfur in the contents of the coke calculated to a coal basis would correspond to about half the sulfur in the original coal. Thiessen¹⁴² found that, in cokes prepared by the Standard A.S.T.M. volatile-matter test from 82 samples including 55 mine face samples and 17 samples of banded coal components, the sulfur in the coke was 83 percent of the sulfur in the coal, and that the sulfur in the coke, calculated back to the original coal basis, was 51.9 percent of the sulfur in the coal. The relationship between the sulfur in the coke and the pyritic and organic sulfur contents of the original coal was found to be $S_{\text{coke}} = 0.62 S_p + 0.45 S_o$.

Bone and Himus¹⁴⁸ reported that a South Australian brown coal which contained 4.8 percent total sulfur and 3.3 percent organic sulfur yielded over 30 percent of the sulfur as mercaptans on carbonization at temperatures over 400° C. At 700° C, 18.9 percent of the sulfur was found as hydrogen sulfide, 30.4 percent as mercaptans, 3.9 percent as tar, and 46.8 percent in the residue. Foerster and Geissler¹⁴⁹ came to different conclusions from those of Powell, finding that, on carbonization of a bituminous coal at 500° C and at 1,000° C, only half of the pyrite and sulfate were decomposed at 500° C, the greater part of the sulfur which was volatilized came from the inorganic compounds,

and the organic sulfur content was practically unchanged. On carbonization of brown coals high in organic sulfur, 70 percent of the total sulfur was expelled as hydrogen sulfide, most of which must have come from organic compounds. Ditz and Wildner¹⁵⁰ tended to support Powell when they found for Arsa coal containing between 8 and 9 percent of sulfur, 96 percent of which was organic, that only half of the original sulfur remained in the coke.

Aronov¹⁵¹ found that at fourteen coke plants the average distribution of sulfur on commercial carbonization was 66.9 percent in the coke, 19.9 percent in the gas as hydrogen sulfide, 0.85 percent in the gas as organic sulfur compounds, 1.95 percent in the tar, 0.79 percent in the aqueous liquor, and 10.4 percent unaccounted for. Woolhouse,¹⁵² using coals of differing sulfur contents, found that pyritic sulfur is decomposed completely at 600° C to ferrous sulfide and hydrogen sulfide, that the organic sulfur yielded hydrogen sulfide and volatile sulfur compounds found in the tar, and that this decomposition was also complete at 600° C. He stated that the sulfur is retained by the coke because of the stability of the ferrous sulfide and the carbon-sulfur complex and its inertness to hydrogen at high temperatures. Lissner and Nemes,¹⁵³ studying the distribution of sulfur in various fractions obtained when coal is carbonized in an atmosphere of nitrogen and steam or with steam alone at temperatures from 200 to 560° C, found that the organic sulfur occurs in four forms. Between 100 and 300° C, sulfur is evolved from phenolic sulfur groups and probably

¹⁴⁷ Sperr, F. W., Jr., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 37-60 (1928).

¹⁴⁸ Bone, W. A., and Himus, G. W., *Coal: Its Constitution and Uses*, Longmans, Green & Co., London, 1936, p. 159.

¹⁴⁹ Foerster, F., and Geissler, W., *Z. angew. Chem.*, **35**, 193-8 (1922).

¹⁵⁰ Ditz, H., and Wildner, H., *Brennstoff-Chem.*, **5**, 149-53 (1924).

¹⁵¹ Aronov, S. G., *Khim. Tverdogo Topliva*, **2**, No. 1, 52-61 (1931).

¹⁵² Woolhouse, T. G., *Fuel*, **14**, 259-64, 286-95 (1935).

¹⁵³ Lissner, A., and Nemes, A., *Brennstoff-Chem.*, **16**, 101-7 (1935).

from $\equiv\text{C}-\text{SH}$ or $\equiv\text{CSSC}\equiv$ groups containing nitrogen. Superheated steam hydrolyzes sulfide sulfur at 380°C and retards the formation of new organic sulfur compounds with the evolution of inorganic sulfur. With the start of tar evolution, hydrogen sulfide appears, the reaction favored by superheated steam and coming from $=\text{CHSH}$ and $=\text{CHSCH}=$ groups. Part of the organic sulfur remaining in the semicoke is oxidizable by nitric acid, and the remainder can be removed only by reduction processes at high temperatures. Wibaut and Stoffel¹⁵⁴ found that from 50 to 60 percent of the organic sulfur in the coal is retained in the coke. Wibaut¹⁵⁵ concluded that part of the organic sulfur remaining in the coke was present in solid solution or held physically by adsorption and that the remainder of the sulfur was retained in chemical combination although it was impossible to isolate such chemical compounds. Wibaut¹⁵⁶ further found that some of the sulfur still retained in coke at $1,000^{\circ}\text{C}$ could be removed at 600°C by treatment with hydrogen. Armstrong and Himus⁵ concluded from the carbonization of high-sulfur bituminous coals that elimination of sulfur under ordinary conditions almost ceases above 700°C , that pyrite is decomposed at low temperatures, that sulfate sulfur is decomposed at low temperatures, that the removal of organic sulfur follows the removal of total sulfur, and that a reduction in pressure during carbonization tends toward retention of sulfur in the coke, particularly at high temperatures. Lowry, Landau, and Naugle,¹⁵⁷ in

making a statistical study of the results of the U. S. Bureau of Mines-American Gas Association Carbonization Assay Tests, found that the data indicated that the sulfur in the dry, ash-free coke was equal to 85 percent of the organic sulfur of the coal plus 86 percent of the pyritic sulfur with a probable error of plus or minus 0.068 percent, the range of values included being as follows:

Sulfur in the coal	0.47 to 4.00
Organic sulfur in the coal	0.32 to 3.63
Pyritic sulfur in the coal	0.01 to 2.00
Sulfur in the coke	0.4 to 3.6

Because the coefficients for the organic and pyritic sulfur were nearly equal and since these data are not always available, and, further, since the correlation coefficient between the sulfur in the coke on a dry basis, S_k , and the total sulfur in the coal as carbonized, S_t , was so high (0.95), they preferred the following simpler relationship, $S_k = 0.084 + 0.759 S_t$. The probable error in this equation was plus or minus 0.065 percent on the dry basis.

Brückner¹⁵⁸ reported that, for brown coals, usually more than half of the sulfur was lost on carbonization, mainly as hydrogen sulfide, and that this loss took place at a lower temperature than for bituminous coals.

The atmosphere present during the carbonization of a coal has a very great influence upon the proportions of sulfur volatilized and remaining in the coke. In general, hydrogen and hydrogen-containing gases tend to increase the amount of sulfur evolved. Snow,¹⁵⁹ for example, found that the effectiveness of removal of sulfur at $1,000^{\circ}\text{C}$ was in the following order:

158 Brückner, H., *Braunkohle*, **27**, 891-3 (1928).

159 Snow, R. D., *Ind. Eng. Chem.*, **24**, 903-9 (1932).

154 Wibaut, J. P., and Stoffel, A., *Rec. trav. chim.*, **38**, 132-58 (1919).

155 Wibaut, J. P., *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 657-73 (1931).

156 Wibaut, J. P., *Z. anorg. allgem. Chem.*, **211**, 398-400 (1933).

157 Lowry, H. H., Landau, H. G., and Naugle, L. L., *Trans. Amer. Inst. Mining Met. Engrs.*, **149**, 297-330 (1942).

Nitrogen	
Carbon dioxide	50 to 60 percent
Carbon monoxide	
Methane and ethane ¹	
Water gas	76 percent
Anhydrous ammonia	82 percent
Hydrogen	87 percent

An instantaneous carbonization in hydrogen gave a removal of 59 percent of the sulfur.

Mangelsdorf and Broughton¹⁶⁰ found that the order of removal increased in the order: carbon monoxide, illuminating gas, steam, hydrogen, and water gas, and commented that their results differ from those of Snow possibly because of the difference in coal. The matter of atmosphere during carbonization is of primary interest in problems concerning the removal of sulfur from coke.

PRODUCTION OF LOW-SULFUR-CONTENT COKE

It is highly desirable and frequently held essential that the sulfur content of coke used for iron blast-furnace operation be low. The A.S.T.M. Specification for Coking Coal¹²⁹ states that the composition of the coking coal shall be such that the dry foundry coke produced therefrom shall not contain more than 1.0 percent sulfur and dry blast-furnace coke not more than 1.3 percent sulfur.

This desire for low-sulfur-content coke has led, first, to the selection of low-sulfur-content coking coals and, second, to the use of cleaned coal. Because the manufacture of blast-furnace coke is one of the major uses for coal and because the quantities of low-sulfur coal are limited, there is a considerable incentive to utilize the higher-sulfur coals. The application of

coal-cleaning methods to coals susceptible of having their sulfur contents reduced has been of great commercial importance as is well known. There are limits, however, to the reduction in sulfur content which can be achieved by these methods. Organic sulfur is not removed by coal-cleaning processes.

Much attention has, therefore, been given to the possible production of low-sulfur-content coke by causing a greater evolution of the sulfur in the volatile matter during coking and elimination of some or all of the residual sulfur in the coke by treatment of the finished coke, usually while still hot. Such investigations go back as far as the 1850's. Investigations along this line have led to few, if any, practical results. The various methods used have been reviewed by Gluud and Jacobson,¹⁶³ Simmersbach,¹⁶¹ Muhlert,²² and Powell and Thompson.¹⁶² The processes for the desulfurization of coke have included the addition of compounds to the coal before coking, the treatment of the hot coke by the passage of various gases through it, and the treatment of the coke either hot or cold with liquid reagents.

Compounds which have been tried as additives to the coal include salt, oxidizing agents, sodium carbonate, lime, and limestone. The salt and the oxidizing agents were supposed to volatilize increased quantities of sulfur, the alkaline materials to bind the sulfur in the form of sulfides to facilitate its absorption by blast-furnace slag. These processes have not achieved commercial success.

Practically all the inexpensive and readily available gases have been tried as media for treating the hot coke, including

¹⁶¹ Simmersbach, O., and Schneider, G., *Kokschemie*, Julius Springer, Berlin, 3rd ed., 1930, pp. 177-86.

¹⁶⁰ Mangelsdorf, T. A., and Broughton, F. P., *ibid.*, **24**, 1136-7 (1932).

¹⁶² Powell, A. R., and Thompson, J. H., *Carnegie Inst. Tech., Coop. Bull.* **7**, 3-13 (1923).

steam, air, nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane, chlorine, coke-oven gas, and producer gas. All have some desulfurizing action, but hydrogen and the gases rich in hydrogen seem to be most effective. Powell¹⁶³ concluded, on the basis of laboratory-scale tests, that "The effect of hydrogen on the removal of sulfur from coke is very noticeable, in most cases the majority of the sulfur being removed during a period of three hours at 1,000° C. With the exception of the decrease in sulfur content, the character of the coke does not seem to be affected by the passage of hydrogen." Gases such as air, carbon dioxide, and steam consume appreciable quantities of coke by combustion and are for that reason impractical.

Some efforts have been made to reduce the sulfur content of coke during dry quenching. The addition of compounds to the coal which would catalytically aid the removal of the sulfur from the hot coke by gases has not proved effective since in all probability the coal already carries a sufficient amount of such compounds. The more recent work along this line merely substantiates the older indications without, however, bringing the problem any closer to commercial solutions.^{159, 160, 164} Some desulfurization of the above type does normally take place in a coke oven as the gases pass from the coking zone through the hot coke already formed on their way out of the oven.

Washing coke with hydrochloric acid has been tried with little, if any, resultant sulfur reduction. Additives intended to convert more of the sulfur to acid-soluble forms have also been ineffective. It ap-

pears that little, if any, desulfurization takes place as a result of the action of water or steam during quenching.

Treatment of the coke to reduce its sulfur content is not practical because of the additional equipment and the relatively long time of treatment required, and, in the treatments with gases, the large volumes of hot gases which must be handled. Cleaning processes which reduce the sulfur content of the coal before it is coked not only make possible the production of coke of lower sulfur content but also at the same time reduce the ash content of the coal and, of course, of the coke also. This decrease in ash content can bring about a further decrease in coke and limestone used in the blast furnace in addition to that brought about by the lowering of the sulfur content. It is probable that some of the increase in efficiency and output of blast furnaces attributed to the lower sulfur content of coke from washed coal may actually be due to the accompanying lower ash content.

There is reason to believe that the importance of the sulfur content of blast-furnace coke is often overestimated. Small differences in the acid-base ratio in the blast-furnace slag may greatly influence the amount of sulfur finally left in the pig iron, the range in variation being greater than that brought about by considerable differences in the sulfur content of the coke.

Simmersbach¹⁶⁵ calculated that, in a blast furnace making 100 tons of pig iron per day and using therefor 120 tons of coke per day, an additional 4.2 tons of limestone is required to remove the sulfur introduced by each 1 percent of sulfur in the coke and that this limestone necessitates the use of an additional 1.30S tons of coke.

¹⁶⁵ See pp. 174-5 of ref. 161.

¹⁶³ Powell, A. R., *J. Ind. Eng. Chem.*, **12**, 1077-81 (1920).

¹⁶⁴ Grünert, E., *J. prakt. Chem.*, N. S. **122**, 1-120 (1929). Kuznetsov, M. I., *Khim. Tverdogo Topliva*, **1**, No. 2, 45-6 (1930).

CHAPTER 13

THE OCCURRENCE OF NITROGEN IN COAL

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Nitrogen is present in all fossil fuels. Its presence is not fortuitous since no completely nitrogen-free coal has yet been found. The nitrogen in coal has the distinction of being the only element present which is exclusively attached in organic combination.¹

The available evidence concerning the occurrence of nitrogen in solid fuels has been obtained in connection with studies involving the origin of coal, the extraction of solid fuels with mineral acids, and the degradation products resulting from thermal or chemical treatment of solid fuels. (For previous summaries dealing with knowledge of nitrogen in coal see references 2 and 3.) The amount of nitrogen contained in ash- and moisture-free fuels of increasing rank is given in Table I.²

TABLE I
NITROGEN CONTENT OF SOLID FUELS²

	Nitrogen percent
Peat	0.7-3.4
Brown coal	0.4-2.5
Bituminous coal	0.6-2.8
Anthracite	0.2-1.5

¹ Schuster, F., *Gas- u. Wasserfach*, **73**, 549-51 (1930).

² Muhlert, F., *Der Kohlenstickstoff*, Wilhelm Knapp, Halle, 1934, p. 1.

It is observed that the figures for each fuel type cover a considerable range. In general, the nitrogen content of bituminous coals is higher than that of brown coals. Bituminous coals contain one to two nitrogen atoms for each hundred atoms of carbon + hydrogen + oxygen. No regularities can be found in the nitrogen content of fuels of the same type, whether arranged in order of age or of occurrence. Although the composition of the coal substance, as regards its carbon, hydrogen, and oxygen content, often varies over wide limits, it varies still more for nitrogen. These deviations occur not only in coals from a definite region or in coals of a certain age, but often also in coals taken from a single field, seam, or even cross section. Thus, the observed deviations in the elementary composition of coals taken from the same shaft and seam are given in Table II and expressed as percentages of the total amount of each element present.³ Samples taken from adjacent positions in a seam may show deviations in their nitrogen content as high as 20 percent.

A possible explanation for these deviations in the nitrogen content of adjacent samples is found in the analysis of the individual morphological constituents.

³ Bertelsmann, W., *F. B. Ahrens' Samml. Chem. u. chem.-tech. Vorträge*, **9**, 329-414 (1904).

TABLE II

DEVIATIONS IN CARBON, HYDROGEN, AND NITROGEN CONTENT OF COALS TAKEN FROM SAME SEAM AND SHAFT ³

	Carbon percent	Hydrogen percent	Nitrogen percent
Minimum	0.5	7.0	21.0
Maximum	6.0	24.0	60.0
Average	3.7	13.0	40.5

Thus, the vitrain, which is usually the main constituent of bituminous coal and which has a humic origin, durain, which has a sapropelic origin, and fusain components of banded coals contain the percentages of nitrogen shown in Table III.⁴

TABLE III

NITROGEN CONTENT OF MORPHOLOGICAL CONSTITUENTS OF COAL ⁴

Nitrogen in	Ruhr Coal			English Coal
	A per- cent	B per- cent	C per- cent	
Vitrain	1.95	1.91	2.02	1.29
Durain	1.57	1.41	1.70	1.03
Fusain	0.60	0.66	0.63	0.95

A second possible explanation for these deviations is the general uncertainty of the determination of nitrogen in coal whether performed by the Kjeldahl or Dumas methods.⁵

THE ORIGIN OF NITROGEN IN SOLID FUELS

It is generally agreed that the nitrogen present in coals has come from plant proteins or animal proteins, or both, which were laid down in earlier eras of the earth. The plants which were concerned with coal

formation are now, with few exceptions, extinct. It is probably reasonable to assume that the composition of these early plants did not greatly differ, chemically, from those of the present and that the products of the decomposition of these early plants would resemble those being formed today. The nitrogen present in solid fuels could not have come solely from wood, since the following figures, based on dry samples, indicate that the nitrogen content of present-day woods is, in general, of a lower order of magnitude than found in coals: ⁶ beech, 0.09; birch, 0.10; fir, 0.05; spruce, 0.04 percent nitrogen, respectively. However, it must be remembered that highly organized plants contain much less nitrogen than the more lowly organized plants. Bacteria contain up to 13 percent, algae 3.2 to 4.8 percent, leaf moss 2.4 to 3.2 percent, ferns 1.6 to 2.4 percent (0.38 percent in the stems, 1.85 percent in the leaves which bear the reproductive organs, 0.72 percent in withered leaves of previous years, and 1.73 percent in fern humus), shave grass 1.6 to 2.4 percent, and typical swamp plants about 1.6 percent nitrogen.⁷

Since coals contain 10 to 30 times the amount of nitrogen which is present in wood one must look for other sources unless, as seems likely,⁸ this nitrogen can be converted into an inert form which permits it to accumulate. The plant proteins, containing 15 to 19 percent nitrogen, are easily attacked by enzymes and converted into amino acids, which, being water soluble, would possibly be partially washed away at the point of their formation or

⁶ Gottlieb, E., *J. prakt. Chem.*, (2) **28**, 385-421 (1883).

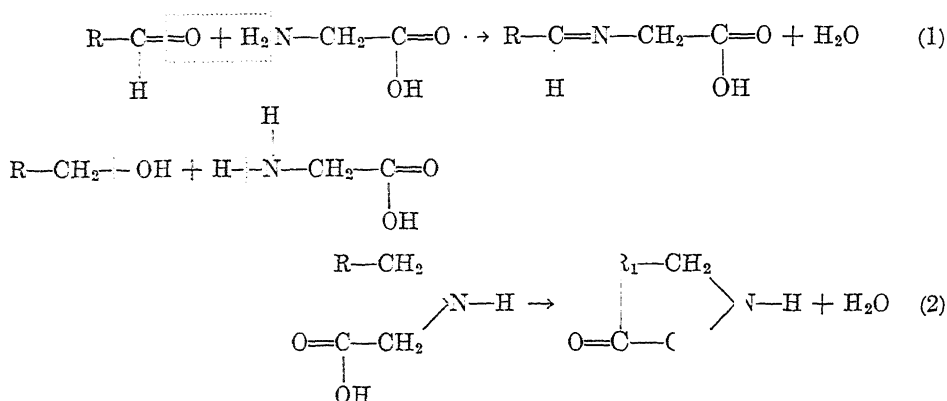
⁷ See p. 4 of ref. 2.

⁴ Fuchs, W., *Die Chemie der Kohle*, Julius Springer, Berlin, 1931, p. 288.

⁵ For a discussion of the difficulties involved in the determination of nitrogen in coal and coke see Kirner, W. R., *Ind. Eng. Chem., Anal. Ed.*, **7**, 294-9 (1935).

⁸ Stadnikoff, G., (a) *Die Chemie der Kohlen*, Ferdinand Enke, Stuttgart, 1931, pp. 30-1; (b) *Die Entstehung von Kohle und Erdöl*, Ferdinand Enke, Stuttgart, 1930, p. 43.

might be attacked by micro-organisms and converted into ammonia, elementary nitrogen, and simpler, nitrogen-free organic compounds. However, part of these amino acids could react with the aldehyde or hydroxyl groups of carbohydrates, which might be formed simultaneously during the decomposition of the plant substance, since monoses, as such, are always present in plant organisms and can be formed readily from polysaccharides, pectins, and cellulose by decomposition of the plant remains.⁹ Thus:



Such reactions can lead to the formation of complex condensation products, reaction 1, with high molecular weights and colloidal properties (so-called melanoids resembling natural humic acids), or to heterocyclic compounds, reaction 2. Maillard also showed that heating these melanoids resulted in their decomposition with the formation of heterocyclic nitrogen compounds. It is possible, by this mechanism, to account for the fact that in an accumulation of plant organisms and their transformation products, for example in a peat bed, the nitrogen content does not decrease with progress in the turification

process but sometimes increases. However, even with this hypothesis it appears that the nitrogen content of the plant substance is still insufficient to explain fully the nitrogen content of coals. The plant substance can supply, at most, only one-tenth to one-thirtieth of the coal nitrogen and so is of minor importance as a source of nitrogen. Some substance high in nitrogen must have been present in the original material from which coal was formed, and this substance was obviously protein. Terres¹⁰ was able to prepare artificial brown coals containing

⁹ Maillard, L. C., *Compt. rend.*, **154**, 66-8 (1912), **155**, 1554-6 (1912), **157**, 850-2 (1913).

¹⁰ Terres, E., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 797-808 (1931).

men containing over 6 percent nitrogen. Terres claimed that the sludge formed from protein putrefaction is the essential material from which coal bitumens are formed and that for the formation of bituminous coals it is necessary to have protein material present along with the lignin, cellulose, waxes, and resins which come from the plant substance. This view explains the fact that bituminous coals generally contain more nitrogen than brown coals.

Animal remains, doubtlessly mixed with large amounts of plant remains, can also furnish proteins which may be responsible for the major part of the nitrogen in coals.¹¹ This has been offered as an explanation for the large variations in the nitrogen content of coal samples taken from adjacent positions in a seam. However, it has been shown¹² that the protein of animal organisms, during decomposition under natural conditions, vanishes completely. Stadnikoff claimed that, since the animal organism contains no appreciable amounts of carbohydrates, the amino acids, formed during the hydrolysis of the animal proteins, could not react to form the complex nitrogen-containing condensation products suggested by Maillard and so the nitrogen is completely removed. However, Stadnikoff apparently completely overlooked the fact that if the animal remains were laid down in the presence of large amounts of plant remains all the conditions would be suitable for the formation of resistant nitrogen-containing complexes which could be retained in the coal.

The amount of nitrogen present in the organic (animal or vegetable) remains is probably not nearly as important as the

ability of this nitrogen to be retained over geological periods of time. A low retentivity would lead to its complete disappearance even if high concentrations were originally present. On the other hand, a high retentivity could lead to an increase in the nitrogen content over a long period of time even though very small concentrations were originally present. Such a theory explains the increasing nitrogen content of peat deposits at increasing depths. For example, the data given in Table IV¹³ indicate this increase in nitrogen content.

TABLE IV

NITROGEN CONTENT OF CAREX PEAT WITH INCREASING TURFICATION¹³

Depth, meters	0.5	1.5	3.5	5.5	7.5	9.5	11.5
Nitrogen, percent	2.35	2.39	2.40	2.58	3.05	2.84	2.69

In considering these figures one must bear in mind what has already been said concerning the strong variations in the nitrogen content of samples taken from adjacent locations.

Another possible source of nitrogen in coals is found in the plant alkaloids.¹⁴ These compounds contain their nitrogen in a cyclic structure and are sufficiently stable to pass through the coalification process without appreciable loss of nitrogen. It has been found¹⁵ that chlorophyll, the green plant coloring matter, can be retained for a long time in a medium of natural fatty acids and their polymerization products (Coorongit). Chlorophyll, being a complex pyrrole derivative, is therefore another substance which can add stable heterocyclic nitrogen-containing molecules to coal. Chlorophyll and other por-

¹¹ See p. 342 of ref. 3.

¹² See pp. 16-7 of ref. 8b. Gregory, W., *Ann.*, **61**, 362-4 (1847); Wetherill, C. M., *Jahresber. Fortschr. Chem. verwandte Theile wiss.*, p. 517 (1855); *J. prakt. Chem.*, **68**, 26-35 (1856); Ebert, R., *Ber.*, **8**, 775 (1875).

¹³ Zailer, V., and Wilck, L., *Z. Moorkultur u. Torfverw.*, **9**, 153-68 (1911).

¹⁴ Thiessen, R., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 214 (1925). See p. 245 of ref. 8b.

¹⁵ See pp. 79-80 of ref. 8a.

phyrins have been detected in coals,¹⁶ which indicates that substances of this type are able to resist decomposition during the coalification process and that temperatures of about 200° C could not have been exceeded during such processes or these compounds would have been decomposed.

Resistant protein materials such as chitin (present in the coatings of bacteria, in fungus cells and micelles, crustaceans, insects, etc.) can also add their nitrogen to coals.¹⁷ Most of the nitrogen present in humus is believed to be in the form of true protein with a different distribution of amino acids, however, from that in plant and animal proteins.¹⁸ When proteins are introduced into soil they are attacked by a great number of micro-organisms and their enzymes and are changed into peptides, amino acids, and finally to ammonia. The ammonia is either oxidized to nitrate or is assimilated by the micro-organisms and changed into microbial protein. The microbial cell substance contains 3 to 10 percent nitrogen. The protein of humus is partly of plant and partly of microbial origin, depending on the extent of the decomposition of the plant residues. The nitrogen content of plant residues is between 0.32 and 2.4 percent; that of humus is 1.3 to 5.6 percent, which shows that a considerable enrichment of protein in the residual organic matter takes place as a result of the decomposition process. The major source of the protein in humus, according to Waksman, is due to the microbial synthesis of nitrogenous substances.

The nitrogen present in humus is not present as free protein or it would be rap-

idly decomposed by micro-organisms. Possibly these nitrogen-containing complexes are closely bound to nonnitrogenous complexes of high carbon content, for instance, lignin, which makes them resistant to attack by micro-organisms.

THE NITROGEN IN HUMIC ACIDS

Humic acids have long been recognized as constituents of the lower-rank coals. Nitrogen is also always associated with the natural humic acids.

The following is a typical analysis for humic acids prepared from Niederlausitzer humic coal:¹⁹ carbon, 60.50; hydrogen, 3.34; nitrogen, 2.03; sulfur, 1.44; ash, 1.96 percent, respectively. Many investigators have looked upon this nitrogen as merely an impurity, largely present in the form of ammonia, presumably as a salt or else firmly adsorbed. This nitrogen, however, is very difficult to remove. By repeated solution and reprecipitation of humic acids, from peat and from soil, it was possible to reduce the nitrogen content from 2.5 to 0.7 percent, but no further.²⁰ By extraction, the nitrogen content of a humic acid was reduced to 0.18 percent.²¹ The preparation of a nitrogen-free humic acid has been reported, using electro-osmosis,²² but oxidative reactions are by no means excluded in such a purification process.²³ In humus, only 2 percent of the nitrogen is removed by heating with calcium hydroxide and 5 percent by heating with potassium hydroxide. This sort of stability is not generally associated with ammonium salts or

¹⁹ Eller, W., and Schöppach, A., *Brennstoff-Chem.*, **7**, 17-20 (1926).

²⁰ Odén, S., *Kolloidchem. Beihefte*, **11**, 75-260 (1919); see also p. 19 of ref. 18.

²¹ Detmer, W., *Landw. Vers.-Sta.*, **14**, 248-300 (1871).

²² Biesalsky, E., and Berger, W., *Braunkohle*, **23**, 197-201 (1924).

²³ See p. 193 of ref. 4.

¹⁶ Treibs, A., *Ann.*, **509**, 103-14 (1934), **510**, 42-62 (1934), **517**, 172-96 (1935).

¹⁷ Keppeler, G., and Hoffmann, H., *Brennstoff-Chem.*, **14**, 41-7 (1933).

¹⁸ Waksman, S., *Humus: Origin, Chemical Composition and Importance in Nature*, Williams and Wilkins Co., Baltimore, 1936, p. 97.

with compounds containing adsorbed ammonia.²⁴

More and more evidence has been accumulating that the nitrogen content of humic acids is mainly ascribable to the presence of proteins associated with them. It is also possible that some of the nitrogen in the humic acids may be bound cyclically. When humic acids are treated with ammonium hydroxide, the ammonia is bound in two ways: (1) easily removable by alkali and (2) nonremovable by alkali.²⁵ The nitrogen in the second form makes up 45 to 60 percent of the total nitrogen present; it is considered to be bound cyclically in the humic acid molecule, possibly the nitrogen having replaced a heterocyclic oxygen atom. Nitrogen bound in this way would be extremely difficult to remove from a complex molecule.

One to five percent nitrogen can be added to artificial cellulose coals by carrying out the pressure coalification in the presence of ammonia.²⁶ The nitrogen thus added must be bound in a manner similar to that in which it is linked in natural coals since this nitrogen is not removed by treatment with hydrochloric acid and, when the artificial nitrogen-containing coal is coked, 60 to 90 percent of the nitrogen remains in the coke.

Lignoprotein complexes prepared from alkaline solutions of lignin and proteins have been compared with humic acids and found similar in most respects.²⁷ It is suggested that the reaction between the lignin and protein molecules involves the amino groups of the protein and the carboxyl, hydroxyl, carbonyl, and methoxyl groups

of the lignin, forming complexes of high stability.

Even though the nitrogen content of plants which were concerned in coal formation is not sufficiently high to explain directly the nitrogen content of solid fuels, it is possible to account for the amount of such nitrogen on the basis of its conversion by reaction with carbohydrates or lignin into complex compounds, melanoids or heterocyclic compounds, which are sufficiently inert to be able to withstand decomposition and thus to have the percentage of nitrogen actually increase. Other resistant compounds include plant alkaloids, porphyrins, and chitin. Also, an increase in nitrogen can be explained by microbial synthesis of nitrogen compounds during the coalification process. It would appear that the types of nitrogen-containing organic compounds which could resist such decomposition would have the nitrogen atoms present in heterocyclic linkages or in a complex molecule in which the nitrogen atoms are protected by the mere complexity of the molecule.

EXTRACTION OF SOLID FUELS WITH MINERAL ACIDS

More direct evidence of the existence of proteins in young fossil fuels has been obtained by extraction methods. Thus, by extraction of soil humus, humic acid preparations, and peat the following substances have been isolated:²⁸

1. Proteins, proteoses, and peptones.
2. Amino acids.
 - (a) Alanine.
 - (b) Leucine.
 - (c) Aspartic acid.
 - (d) Isoleucine.
 - (e) Proline.
 - (f) Asparaginic acid.
 - (g) Glutamic acid.

²⁴ See p. 141 of ref. 18.

²⁵ Fuchs, W., and Leopold, H., *Brennstoff-Chem.*, **8**, 73-7 (1927).

²⁶ Berl, E., *Angew. Chem.*, **45**, 517 (1932).
Proc. 3rd Intern. Conf. Bituminous Coal, **2**, 820-33 (1931).

²⁷ See pp. 188-90 of ref. 18.

²⁸ See pp. 141-9 of ref. 18. Suzuki, S., *Bull. Coll. Agr. Tokyo*, **7**, 513-29 (1907).

- (h) Tyrosine.
- (i) Histidine.
- (j) Arginine.
- (k) Lysine.
- 3. Amides.
 - (a) Urea.
- 4. Amines.
 - (a) Trimethyl amine.
 - (b) Choline.
 - (c) Creatinine.
- 5. Purine bases.
 - (a) Xanthine.
 - (b) Hypoxanthine.
 - (c) Adenine.
 - (d) Guanine.
 - (e) Cyanuric acid.
- 6. Pyrimidine derivatives.
 - (a) Cytosine.
- 7. Pyridine derivatives.
 - (a) α -Picoline- γ -carboxylic acid.
- 8. Chitin.
- 9. Nucleic acids.

The isolation of these products proves quite definitely the protein nature of the nitrogen in the younger fossil fuels. A Michigan brown peat, containing 2.25 to 2.75 percent nitrogen in an oven-dried state, lost very little of its nitrogen when extracted with boiling water. By means of dilute (33 percent) mineral acids (hydrochloric or sulfuric acids), at the boiling point, 50 to 60 percent of the nitrogen was extracted in 30 to 60 hours. By continuing the process essentially to completion it was finally possible to extract 6S percent of the nitrogen present.²⁹ The amount of nitrogen extracted was a function of the strength of the acid used, the period of extraction, and the particle size of the peat. By analysis the nitrogen in the extract was divided into groups as shown in Table V. A weathered brown peat, containing 2.69 percent nitrogen, gave similar figures except that no diamino acid nitrogen was present and the monoamino acid nitrogen increased accordingly. Jodidi's work has

TABLE V

TYPES AND AMOUNTS OF NITROGEN COMPOUNDS
IN A PEAT EXTRACT ²⁹

	Percent Nitrogen Extracted Based on	
	Total Nitrogen Present	Nitrogen Extracted
Amide nitrogen	16.02	26.80
Monoamino acid nitrogen	39.05	65.68
Diamino acid nitrogen	2.96	5.00
Total	58.03	97.48

been extended to include lignite, subbituminous, bituminous, and anthracite coals, containing, respectively, 0.87, 1.68, 1.44, and 1.36 percent nitrogen.³⁰ The fuels were all air dried and extracted for 72 hours by refluxing with 33 percent sulfuric acid. The peat extract was brown, the lignite extract was straw colored, and all the other extracts were colorless. It was found that if the subbituminous coal was ground to pass a 30-mesh sieve further grinding did not increase the yield of extract. The results are summarized in Table VI.

Table VI shows a continuous decrease in the quantity of extractable nitrogen in the series from peat to anthracite, a large percentage of the total nitrogen of peat being extractable and a small percentage from anthracite. Likewise the amount of amide nitrogen extracted continuously diminishes in the series from peat to anthracite, a considerable proportion of the nitrogen in peat being in amide form. There is also a general diminution in the monoamino acid nitrogen in going from peat to anthracite. Diamino acid nitrogen is determinable only for peat and lignite, apparently being absent in the bituminous and anthracite coals.

These same authors similarly studied the

²⁹ Jodidi, S. L., *J. Am. Chem. Soc.*, **32**, 396-410 (1910), **33**, 1226-41 (1911), **34**, 94-9 (1912).

³⁰ Shacklock, C. W., and Drakeley, T. J., *J. Soc. Chem. Ind.*, **46**, 478-81T (1927).

TABLE VI

TYPES AND AMOUNTS OF NITROGEN COMPOUNDS IN THE EXTRACTS OF VARIOUS FUELS ³⁰

	Nitrogen in				
	Peat percent	Lignite percent	Subbitu- minous percent	Bitumi- nous percent	Anthracite percent
Total present	3.10	0.87	1.68	1.44	1.36
Extracted {	Amide	0.72	0.034	0.019	0.005
	Monoamino acid	1.20	0.074	0.079	0.031
	Diamino acid	0.52	0.082	Trace	Nil
Total extracted	2.44	0.190	0.098	0.078	0.036
Percentage of total nitrogen present extracted	78.5	21.8	5.8	5.41	2.64

top, middle, and bottom parts of a Lancashire bituminous coal seam in order to determine the effect of comparatively shorter geological periods on the division and extractability of nitrogen (see Table VII).

TABLE VII

TYPES AND AMOUNTS OF NITROGEN COMPOUNDS IN A BITUMINOUS COAL TAKEN FROM VARIOUS DEPTHS ³⁰

	Nitrogen in		
	Top percent	Middle percent	Bottom percent
Total present	1.33	1.33	1.34
Extracted {	Amide	0.021	0.026
	Monoamino acid	0.064	0.044
	Diamino acid	0.000	0.000
Total extracted	0.085	0.070	0.072
Percentage of total nitrogen present extracted	6.38	5.26	5.37

Some suggestion of the effect of age is shown by the fact that the greatest amount of nitrogen was extracted from the top, presumably the youngest sample, but the remaining figures do not warrant the drawing of any such conclusion. Hence, the more radical changes observed in the state of nitrogen in peat, lignite, bituminous

coal, and anthracite have been effected during a longer geological period than that required for the deposition of a single seam.

The series of fossil fuels from peat through anthracite represents humus formations which have undergone extensive decomposition for periods of many years. The age of peats ranges from a few years to several thousands of years. Coal deposits are much older, some being of the order of a million and others more than a hundred million years old. From the figures presented by Shacklock and Drakeley it would appear that in the coalification process nitrogen, originally present as amino or amide groups, is converted to some other nonbasic form which is incapable of being extracted by means of mineral acids.

The results of the extraction of solid fuels with mineral acids indicate that only from the younger fuels is it possible to remove directly nitrogen-containing compounds. Such extractable substances include proteins and their hydrolysis products together with amines, amides, and basic heterocyclic nitrogen compounds. The nitrogen present in the older fuels cannot be extracted with mineral acids;

this is also true for crude petroleum. A reasonable explanation for this behavior is that during coalification the reactive amino and imino groups, which are present in the younger fuels, are involved in reactions with other groups such as carboxyl, hydroxyl, carbonyl, and methoxyl, which convert the basic groups into nonbasic groups, the nitrogen being either held in a heterocyclic linkage or else linked linearly between units of such complexity or negativity that the nitrogen loses its basic properties.

In the higher-rank fuels, there is really no direct evidence as to the manner in which the nitrogen is held. Most of the meager information we have is based on studying the products derived from the fuel after it has been subjected to some degradation process such as: (1) solvent extraction, (2) vacuum distillation, (3) low- and (4) high-temperature distillation, (5) gasification, (6) combustion, (7) oxidation, (8) hydrogenation, (9) halogenation, or (10) hydrolysis, all of which alter the original structure of the coal. However, certain conclusions can be drawn as to the probable type of nitrogen linkage in the original coal from a study of these degradation products.

SOLVENT EXTRACTION

A French bituminous coal, from Montrambert, Loire, yielded with boiling benzene about 0.1 percent of extract which, when shaken with dilute sulfuric acid, gave such small amounts of bases that they were not further investigated.³¹ The same authors also mentioned that bituminous coal yielded practically no extract when treated with dilute acids, indicating the absence of basic material in the original coal. A large-scale benzene extraction was carried out on

a Saar, Maybach, coal.³² Fifty-two hundred kilograms of coal yielded 10.63 kilograms of extract (not including 2.67 kilograms of benzene-soluble petroleum-ether-insoluble material), which corresponded to a 0.22 percent yield. This material contained 0.5 percent of basic compounds, isolated by extraction with dilute hydrochloric acid. Four hundred cubic centimeters of the crude extract was shaken with dilute hydrochloric acid which, after evaporation, gave 0.5 gram of crystalline hydrochlorides. On steam distillation, after addition of alkali, there was obtained a steam-volatile and a steam-nonvolatile fraction of bases. The former was an oily liquid, slightly soluble in water, with an odor resembling that of dihydropyrroles; when treated with nitrous acid and then subjected to the Liebermann reaction, this oily liquid gave a positive test indicating the presence of secondary amines. A solid *o*-nitrobenzoyl derivative was prepared, m.p. 110° C, which on analysis indicated the base to have the empirical formula $C_7H_{13}N$, so that the compound was possibly an alkylated dihydropyrrole. The steam-nonvolatile base was amorphous, colorless, and odorless.

A thorough study of the solvent extraction of a Pittsburgh bituminous coal using benzene, aniline, tetralin, and phenol has been carried out.³³ The effect of the variables time and temperature was studied and, with benzene, the additional variable of particle size. The sized coal contained 1.63 percent nitrogen and the μ -coal 1.90 percent nitrogen (on a dry basis). The bases from the extract were removed with 2 *N* hydrochloric acid, the solution was made alkaline with sodium hydroxide, and the free bases were recovered by ether ex-

³¹ Pictet, A., Ramseyer, L., and Kaiser, O., *Compt. rend.*, **163**, 358-61 (1916). Pictet, A., *Ann. chim.*, (9) **10**, 249-330 (1918).

³² Pictet, A., and Ramseyer, L., *Ber.*, **44**, 2486-97 (1911).

³³ Asbury, R. S., *Ind. Eng. Chem.*, **26**, 1301-6 (1934), **28**, 687-90 (1936).

traction. The results are given in Table VIII. When the 16–20 mesh coal was preheated at 350° C and then extracted at 260° C with benzene the yield of bases was increased to 0.93 percent, and when preheated at 400° C and extracted at 260° C

TABLE VIII

YIELD OF EXTRACT AND BASES FROM BENZENE PRESSURE SOXHLET EXTRACTION OF A PITTSBURGH BITUMINOUS COAL AT 260° C³³

Coal size, mesh	4–8	16–20	60–80	μ
Total time of extractions, hours	47	44	38	302
Yield of extract at end of run (dry, ash-free), percent	15.5	17.8	18.0	28.7
Bases, percent of extract	0.59	0.61	0.38	0.5
Bases, percent of coal	0.09	0.11	0.07	0.14

the yield of bases was further increased to 2.30 percent of the extract. It was believed that this increase occurred at the expense of the neutral ether-insoluble portion of the extract due to thermal decomposition.

Similar data for the extraction of the same coal (16–20 mesh) with the other solvents mentioned above are given in Table IX. The results indicate that pressure extraction of coal with various solvents at elevated temperatures removes only small amounts of basic material soluble in dilute hydrochloric acid. Unfortunately, no elementary analyses are available for this material. However, the fact that pressure solvent extraction removes any basic ma-

terial is in agreement with the idea that solvent extraction is in reality a very mild process of thermal decomposition.³⁴

Pyridine extraction of a coal at 90° C removed 0.74 percent of bases (calculated from the weight of extract), or 0.076 percent of bases (calculated from the weight of coal used).³⁵ As it was admitted that the product contained considerable amounts of pyridine, this figure is undoubtedly high.

A "gas flame" coal was extracted with tetralin at 250° C under 6.5 atmospheres pressure.³⁶ In 18 hours a 20.3 percent yield of extract was obtained which contained 0.034 percent of bases; this corresponds to a yield of 0.007 percent of bases calculated on the amount of coal used.

VACUUM DISTILLATION

Pictet has also studied vacuum distillation of coal.³¹ This was considered to be a more practical method than solvent extraction for investigating coal since it is faster and gives better yields. From 30 kilograms of coal heated to 450–500° C at 15–17 millimeters a 4 percent yield of vacuum tar was obtained.³⁷ This tar, on extraction with dilute acid, yielded "consider-

³⁴ Lowry, H. H., *Ind. Eng. Chem.*, **26**, 133–9 (1934).

³⁵ Hofmann, F., and Damm, P., *Brennstoff-Chem.*, **3**, 73–9, 81–91 (1922).

³⁶ Berl, E., and Schildwächter, H., *ibid.*, **9**, 105–13 (1928).

³⁷ Pictet, A., and Bouvier, M., *Ber.*, **46**, 3342–53 (1913).

TABLE IX

YIELD OF EXTRACT AND BASES FROM THE PRESSURE SOXHLET EXTRACTION OF A PITTSBURGH BITUMINOUS COAL³³

Solvent	Aniline	Tetralin (Cumulative)				Phenol
Temperature, °C	225	250	300	350	400	250
Total time of extraction, hours	464	136	126	108	4	65
Total extract, percent	47	33.8	50.8	81.6	85.5	66.7
Bases (percent of extract)	1.30	0.5	0.9	1.5	2.6	0.2
Bases (percent of coal)	0.61	0.17	0.46	1.22	2.22	0.13

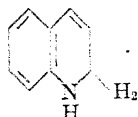
TABLE X
 BASES FROM VACUUM TAR³⁸

Compound	Empirical Formula	General Formula	Boiling Point °C	Melting Point of Picrate °C
1	C ₇ H ₉ N *	C _n H _{2n-5} N	198-203	170
2	C ₈ H ₇ N †	C _n H _{2n-9} N †‡	225	195
3	C ₉ H ₉ N	C _n H _{2n-9} N †	247-250	184
4	C ₁₀ H ₁₁ N	C _n H _{2n-9} N †	250-260	184
5	C ₁₁ H ₁₃ N	C _n H _{2n-9} N †	260-265	173
6	C ₁₂ H ₁₅ N	C _n H _{2n-9} N †	270-280	166

* Probably a mixture of toluidines since it consisted of primary aromatic amines which could be diazotised and coupled with β -naphthol.

† Isomeric with indole.

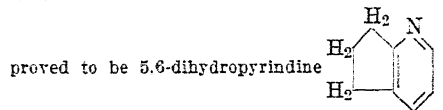
‡ Compounds 2-6 all belonged to series C_nH_{2n-9}N, which is that, e.g., of dihydroquinoline,



These were all colorless liquids, insoluble in water, and were unsaturated secondary

amines. They had odors resembling quinoline and its homologs.

§ A base, C₈H₉N, has been isolated from Fushun shale tar.³⁹ This compound belongs to the series C_nH_{2n-7}N, which is intermediate between the above series. This base was later synthesized⁴⁰ and



proved to be 5,6-dihdropyridine, which has the following physical properties: b.p.

199° C_{760mm}; 1.5407; picrate, m.p. 181-182° C.

able amounts of basic constituents, among which secondary bases seemed to predominate."

From 1.5 tons of coal, Montrambert, Loire, 60 kilograms of vacuum tar was obtained by heating the coal to a maximum temperature of 450° C at 15-20 millimeters.^{32,35} The nitrogen-containing bases of vacuum tar, which constituted 0.2 percent of the tar, were separated by extraction of the tar with dilute hydrochloric acid. Owing to the small quantity of bases available, it was possible to determine only the elementary composition of fractions which were obtained by distillation and to determine the melting points of their picrates. Some of Pictet's data are shown in Table X.

Pictet stated that the above bases seemed to contain an unhydrogenated benzene ring. He believed that the bases were formed by thermal decomposition of nitrogen-containing substances in the coal and that the bases did not exist, as such, in the coal. The bases isolated from vacuum tar were different from those obtained from the benzene extraction of coal. Since only small quantities of these bases were formed and since no ammonia was produced during the vacuum distillation, nearly all the nitrogen of the coal remained in the vacuum coke.

³⁸ Pictet, A., Kaiser, O., and Labouchere, A., *Compt. rend.*, **165**, 113-16 (1917).

³⁹ Eguchi, T., *Bull. Chem. Soc. Japan*, **2**, 176-86 (1927), **3**, 227-43 (1928).

⁴⁰ Thompson, W. C., *J. Am. Chem. Soc.*, **53**, 3160-4 (1931).

The majority of the bases, like the hydrocarbons and alcohols obtained from the benzene extract and from the vacuum tar, were hydroaromatic. Whereas the bases isolated from the two preparations were apparently different, the hydrocarbons and alcohols from the two different sources were apparently identical. Pictet compared the physical properties of such hydrocarbons with those reported by Mabery⁴¹ from Canadian petroleum and found a very close agreement. The agreement was not so close for hydrocarbons from Caucasian, Ohio, or California petroleums. Certain of the hydrocarbons from the benzene extract of Pictet exhibited optical activity, as do certain petroleum hydrocarbons; those from vacuum tar were optically inactive.

In connection with the similarity between the compounds in petroleum and those obtained from the vacuum distillation and benzene extraction of coal, it is interesting to consider recent knowledge concerning the occurrence of nitrogen in petroleum. A study of the nitrogen compounds in petroleum has been under way at the University of Texas since 1926 as part of the research project of the American Petroleum Institute.⁴² To date, nothing is known of the structure of the nitrogen in *crude, undistilled petroleum*. Very little, if any, of the nitrogen in petroleum can be extracted from crude oil with dilute mineral acids; this is analogous to the result obtained with the higher-rank coals. Hence, it is concluded that the nitrogen in petroleum

is present in the form of nonbasic compounds of unknown structure. However, when petroleum is distilled the *distillate* contains both basic and nonbasic nitrogen compounds, the basic being produced as a result of thermal decomposition, but the nonbasic predominate. It is not possible to extract quantitatively the nitrogen compounds from crude petroleum or from its distillation products by means of dilute mineral acids.

In this investigation the kerosene fraction of an asphalt-base petroleum from the McKittrick field in the San Joaquin valley in California has been used. The crude petroleum contained 0.64 percent nitrogen and the kerosene distillate contained 0.055 percent nitrogen. One hundred and fifty barrels of residue, left after liquid sulfur dioxide extraction of the kerosene distillate, was extracted with dilute sulfuric acid, giving 50 liters of water-insoluble bases, called "kero bases," which were used in the investigation; 80,000 barrels of this petroleum yielded one barrel of kero bases. Approximately 55 percent of the nitrogen compounds in the kerosene distillate could be extracted with dilute sulfuric acid. In the higher-boiling distillates, containing a greater total nitrogen content, the proportion of basic to nonbasic compounds decreased with increase in temperature at which the fractions were collected. It was found that the ratio of aromatic to nonaromatic types present in the kero bases was 15 to 85. The common coal-tar bases, quinoline, isoquinoline, quinaldine, and lepidine, were absent, although special attempts were made to find them.

In the lower-boiling fractions pyridine homologs are probably present. By using a *cracked gas oil* and *cracked residuum* from California petroleum, the temperature of cracking being 454°C at 54 to 58 atmospheres, the following nine bases were

⁴¹ Mabery, C. F., et al., *Am. Chem. J.*, **19**, 374-81, 419-85, 796-804 (1897), **25**, 253-307 (1901).

⁴² Bailey, J. R., et al., *Ind. Eng. Chem.*, **20**, 83-5 (1928); *J. Am. Chem. Soc.*, **52**, 1239-50 (1930), **53**, 1002-11 (1931), **55**, 4186-40, 4141-2, 4143-5, 4145-9 (1933), **56**, 2741-3 (1934), **59**, 175-7, 2449-50 (1937), **60**, 763-5, 3025-8, 3028-32 (1938), **61**, 1017-9, 2609-15 (1939), **62**, 1967-9 (1940), **63**, 637-41 (1941). Dunstan, A. E., Nash, A. W., Tizard, H., and Brooks, B. T., *The Science of Petroleum*, Oxford University Press, Vol. I, 1938, pp. 1047-52.

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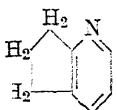
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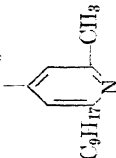
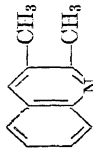
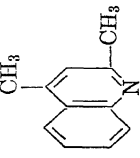
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THE OCCURRENCE OF NITROGEN IN COAL

 TABLE XI
 NITROGEN COMPOUNDS FROM PETROLEUM DISTILLATES 42

Name	Empirical Formula	General Formula	Structure	Boiling Point °C	Melting Point	N_D	D	Melting Point of Picrate °C
Alkylated dihydropyridine or cyclohexyl (or methylcyclopentyl) dihydrodimethylpyridine	$C_{13}H_{23}N$	$C_nH_{2n-6}N$	225.6 ₇₆₀	24.5	$N_D^{20} = 1.4850$	$D_4^{20} = 0.8700$	158.7
Alkylated cyclohexyl- or cyclopentylpyridine	$C_{16}H_{23}N$	$C_nH_{2n-7}N$		278.2 ₇₆₆	23-24.3	$N_D^{20} = 1.5120$	$D_4^{20} = 0.9391$	151
2,3-Dimethylquinoline	$C_{11}H_{11}N$	$C_nH_{2n-11}N$		273 ₇₆₀	67	231
2,4-Dimethylquinoline	$C_{11}H_{11}N$	$C_nH_{2n-11}N$		274 ₇₆₆	194

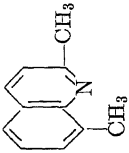
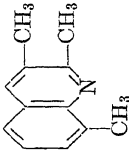
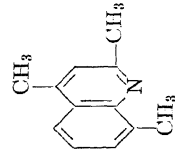
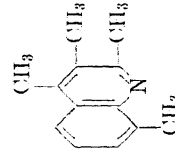
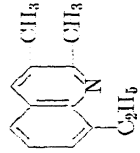
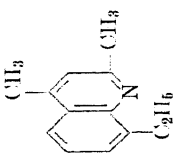
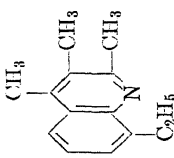
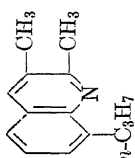
2,8-Dimethylquinoline	$C_{11}H_{11}N$	$C_nH_{2n-11}N$		252.4764	24	$n_D^{25} = 1.5997$
2,3,8-Trimethylquinoline	$C_{12}H_{13}N$	$C_nH_{2n-11}N$		280.747	55-6	$n_D^{50} = 1.5828$	242-5
2,4,8-Trimethylquinoline	$C_{12}H_{13}N$	$C_nH_{2n-11}N$		280.746	43	$n_D^{50} = 1.5855$	193
2,3,4,8-Tetramethylquinoline	$C_{13}H_{15}N$	$C_nH_{2n-11}N$		77-8	240 (dec.)
2,3-Dimethyl-8-ethylquinoline	$C_{13}H_{15}N$	$C_nH_{2n-11}N$		284.6765	36.5	$n_D^{20} = 1.5940$	$D_4^{20} = 1.017$	220 (dec.)

TABLE XI—Continued
NITROGEN COMPOUNDS FROM PETROLEUM DISTILLATES 42

Name	Empirical Formula	General Formula	Structure	Boiling Point °C	Melting Point °C	N_D^{25}	D_4^{20}	Melting Point of Pierate °C
2,4-Dimethyl-8-ethylquinoline	$C_{13}H_{16}N$	$C_nH_{2n-11}N$		288-297	$N_D^{25} = 1.5846$	$D_4^{20} = 1.017$	165-6
2,3,4-Trimethyl-8-ethylquinoline	$C_{14}H_{17}N$	$C_nH_{2n-11}N$		320	52.5-53	$N_D^{25} = 1.5798$	216
2,3-Dimethyl-8-n-propylquinoline	$C_{14}H_{17}N$	$C_nH_{2n-11}N$		299.5	14.5-15.5	$N_D^{25} = 1.5778$	$D_4^{20} = 0.9996$	198-9

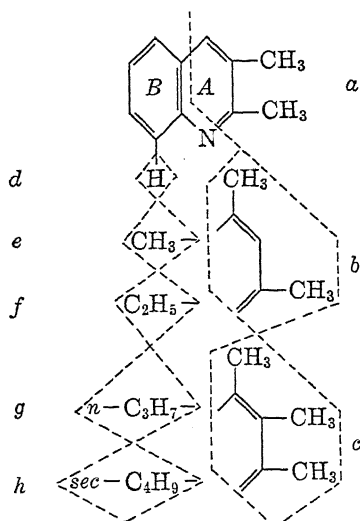
VACUUM DISTILLATION

2,4-Dimethyl-8- <i>n</i> -propyl-quinoline	<chem>Cc1ccc2c(c1)c(C)nc(C)cc2CCC</chem>	298-747	$N_D^{25} = 1.5748$	$D_4^{20} = 0.9992$
2,3,4-Trimethyl-8- <i>n</i> -propyl-quinoline	<chem>Cc1ccc2c(c1)c(C)c(C)nc(C)cc2CCC</chem>	330	69-70	$N_D^{20} = 1.5618$	211-11.5
2,4-Dimethyl-8- <i>sec</i> -butyl-quinoline	<chem>Cc1ccc2c(c1)c(C)nc(C)cc2CCCC</chem>	310	$N_D^{20} = 1.5669$	$D_4^{20} = 0.9824$	148-50
Transformer oil bases; are not quinolines but probably polynuclear types, e.g., acridine or naphthoquinoline	<chem>Cc1ccc2c(c1)c(C)nc(C)cc2</chem>	83.5-84	$N_D^{20} = 1.6570$ (<i>crude</i>)	228.5-29.5
	<chem>Cc1ccc2c(c1)c(C)nc(C)cc2</chem>	86-87	228-29

isolated: 2- and 4-methylpyridine; 2,4-, 2,5-, 2,6-, and 3,5-dimethylpyridine; 2,4,6-trimethylpyridine; quinoline; and 2-methylquinoline. No nonaromatic types, such as are predominantly present in *straight-run distillates*, are encountered in *cracked distillates*; the latter contain only aromatic types. The aromatic types are obviously pyrolysis products of more complex molecules. The nonaromatic bases are evidently unstable at the cracking temperature and undergo dealkylation, dehydrogenation, and molecular rearrangement, forming more stable aromatic types. Analogously, the presence of nonaromatic bases along with aromatic bases in bituminous coal tar has been suspected since the isolation of dihydroacridine, $C_{13}H_{11}N$, from a sample of crude acridine.⁴³ Table XI lists the compounds whose structures have been determined after isolation from the kerosene distillate of California petroleum.

It may be observed that the majority of these compounds are alkylated quinolines, all of which are methylated in the 2-position, the other positions bearing methyl (or higher alkyl groups) being the 3-, 4-, and 8-positions. So far, no compounds have been found with alkyl groups in the 1-, 5-, 6-, or 7-positions. The pyridine nucleus contains only methyl groups while the benzene nucleus so far has been found to contain, in position 8-, the methyl, ethyl, *n*-propyl, and *sec*-butyl groups. The following diagram represents 12 of the 13 quinoline homologs isolated to date. 2,3,4-Trimethylquinoline (*AcBd*) has not been found, although a special attempt was made to find it. 2,8-Dimethylquinoline is not represented in the diagram.

Bailey also pyrolyzed cottonseed meal in the presence of lubricating oil, finally heating the mixture to red heat, to test the as-



sumption that petroleum originates from animal or vegetable protein, with carbohydrates and fats contributing to the formation of the nitrogen compounds present.⁴⁴ It was found that the bases obtained from the pyrolyzed products represented as complex a mixture as is present in the petroleum bases. However, the cottonseed meal bases were at least 50 percent petroleum ether-insoluble and the higher-boiling fractions contained compounds with more than one nitrogen atom per molecule. There was also no evidence for naphthenic compounds such as are present in the petroleum bases. The lower-boiling fractions contained pyridine and various alkylated pyridines, identical with those obtained from the distillation of coal, shale, or bones; the coal-tar bases, quinoline, isoquinoline, quinaldine, and lepidine, were also found. The kero base, 2,3,8-trimethylquinoline, was likewise isolated.

The molecular distillation in high vacuum (0.001 millimeter) of the same coal used by Asbury³³ has been carried out and

⁴³ Decker, H., and Dunant, G., *Ber.*, **42**, 1178-9 (1909).

⁴⁴ Bailey, J. R., et al., *J. Am. Chem. Soc.*, **58**, 1097-1104 (1936).

a study made of the variables—heating rate, exhaustive stepwise treatment, coal particle size, and pressure—on the composition and yield of products.⁴⁵ It was found that very little distillate appeared until temperatures above 350° C were attained and hence none of the substance which distilled and condensed had existed, as such, in the original coal; that is, the condensate consisted of substances which were formed as a result of the thermal decomposition of the coal. The same coal was distilled from a standard Fischer aluminum retort while the apparatus was being swept with a stream of nitrogen. The data thus obtained permit a comparison of the effect of reduced pressure on the yield of condensate and on the amount of bases produced with those obtained at atmospheric pressure. The maximum temperature attained under both conditions of pressure was about 525° C. The bases present in the distillates were extracted with 2 *N* hydrochloric acid, the acid extract neutralized with potassium hydroxide solution, and the free bases removed with ether. The data are given in Table XII.

It is observed that the quantity of bases

obtained by this method is of the same order of magnitude as that obtained by pressure solvent extraction. Since vacuum distillation involves somewhat more vigorous thermal decomposition than solvent extraction, it would be expected that vacuum distillation would yield somewhat larger amounts of bases.

Solvent extraction and vacuum distillation experiments on solid fuels indicate that these processes cause mild thermal decomposition. The isolable bases are not present as such even in small amounts but are formed from complex molecules by thermal reactions involving dealkylation, molecular rearrangement, and partial dehydrogenation. The evidence so far obtained indicates that such bases consist predominantly of secondary cyclic amines, possibly alkylated dihydroquinolines or pyrroles, in which the benzene nucleus is unhydrogenated while the pyridine or pyrrole nucleus is hydrogenated at the double linkage between the nitrogen and carbon atoms.

Present information concerning the nitrogen compounds in petroleum agrees fairly well with what is known regarding the nitrogen compounds in coals of higher rank than lignites. Appreciable quantities of bases cannot be extracted either from petroleum or from the coals with mineral acids. Mild thermal treatment of both fuels results in the formation of simpler nitrogen-containing compounds, some of which are extractable with mineral acids and in which the nonaromatic types predominate. By more drastic thermal treatment both fuels yield the same purely aromatic bases, namely, pyridines, quinolines, isoquinolines, etc.

TABLE XII

COMPARISON OF YIELDS OF CONDENSATE AND OF BASES PRODUCED IN VACUUM DISTILLATION AND FISCHER RETORT DISTILLATION OF A PITTSBURGH ⁴⁶ BITUMINOUS COAL

	Vacuum		Fischer
	20-40	20-40	Retort
	mesh	μ-Coal	mesh
Condensate, percent	21.7	26.0	18.0
Bases (percent of condensate)	0.91	0.58	2.3
Bases (percent of coal)	0.20	0.16	0.4

⁴⁵ Juettner, B., and Howard, H. C., *Ind. Eng. Chem.*, **26**, 1115-8 (1934). *Coal Research Lab., Carnegie Inst. Tech. Bull.* **8** (1934), 22 pp.

LOW-TEMPERATURE DISTILLATION

The above figures for the Fischer retort distillation are an indication of the amount of volatile bases formed in a low-tempera-

ture distillation. Usually the nitrogen bases of low-temperature tar constitute less than 5 percent of the tar. Table XIII shows the distribution of nitrogen among the products obtained from the low-temperature distillation of various solid fuels.

TABLE XIII

DISTRIBUTION OF NITROGEN AMONG THE PRODUCTS OF LOW-TEMPERATURE DISTILLATION

	Bituminous Coal		Brown Coal ⁴⁶	Peat ⁴⁷		
	A ⁴⁶	B ⁴⁷		Leber- mudde	Low Moer	High Moer
Temperature of distillation, °C	550	575	550	520	520	520
Percentage of total nitrogen in:						
Coke	82.6	66.1	67.5	54.1	73.3	58.2
Tar	15.9	4.4	4.4	13.3	6.1	3.4
Gas (as N ₂)	10.8	27.1	14.3	6.1	28.5
Ammonia	1.1	1.8	1.0	18.3	14.5	9.9
Pyridine	0.4
Total	99.6	83.5	100.0	100.0	100.0	100.0

In bituminous coal B, on subsequent heating of the semicoke, an additional 16 percent of the total nitrogen was converted into ammonia, which brings the ammonia figure to approximately that obtained in commercial coking or illuminating-gas practice. (See Table XIX.) Gluud and Breuer⁴⁷ pointed out that the sum of the directly determined components reached a figure of only 83.5 percent. If they had calculated the value for elementary nitrogen by difference, as is customary and as was done in the other work reported above, this figure would have been 27.3 instead of 10.8 percent. However, the amount of elementary nitrogen was experimentally determined and must be approximately correct. This large deviation is ascribed to errors in the determination of nitrogen in the coal and coke by either the Kjeldahl or

Dumas method.⁵ The determined values are probably low, and a negative error of about 0.5 percent in the coke-nitrogen determination would suffice to explain the 16.5 percent discrepancy in nitrogen since each 0.1 percent of nitrogen in the coke, owing to the large factor involved, would cause an error of 4 percent in the nitrogen balance. The organic nitrogen-containing compounds in low-temperature coke begin to decompose at temperatures above 600° C with the formation of ammonia. In high-temperature coking the major part of the ammonia is evolved at temperatures above 600° C.⁴⁸

The United States Bureau of Mines⁴⁹ has carried out the carbonization of 55 American coals and various blends of these coals at temperatures ranging from 500 to 1,100° C and analyzed the products obtained. An analysis of these data has been made;⁵⁰ the results, so far as they concern the nitrogen in the coals and their carbonization products, can be summarized as follows: The volatile nitrogen can be calculated from the equation:

$$N_v = N_c - (N_c + C)Y$$

where N_v = volatile nitrogen.

N_c = nitrogen in the coal, as charged

C = a constant.

$$Y = \frac{\text{yield of coke}}{100}$$

⁴⁸ Fischer, F., and Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 215-26 (1918).

⁴⁹ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph* **5** (1934), 164 pp. Fieldner, A. C., Davis, J. D., et al., *U. S. Bur. Mines, Tech. Papers* **570** (1936), 34 pp., **571** (1936), 33 pp., **572** (1937), 50 pp., **584** (1938), 81 pp., **595** (1939), 83 pp., **594** (1939), 43 pp., **596** (1939), 46 pp., **599** (1939), 38 pp., **601** (1939), 45 pp.; *Bull.* **411** (1938), 162 pp.; *Rept. Investigations* **3428** (1939), 32 pp.

⁵⁰ Lowry, H. H., Landau, H. G., and Naugle, Leah L., *Trans. Am. Inst. Mining Met. Engrs.*, **149**, 297-326 (1942).

⁴⁶ Strache, H., and Frohn, E., *Brennstoff-Chem.*, **3**, 337-40 (1922).

⁴⁷ Gluud, W., and Breuer, P. K., *Ges. Abhandl. Kenntnis Kohle*, **3**, 227-37 (1918).

LOW-TEMPERATURE DISTILLATION

Also,

$$Y = A + B \text{ (Fixed carbon in coal)} \\ \qquad \qquad \qquad + \text{Ash in coal)}$$

where A = a constant.

$$B = a \text{ constant } (0.79).$$

The constant A decreases with increasing temperature, whereas B is independent of temperature. The factor $(N_C + C)Y$ represents the calculated nitrogen in the coke. It is noted that the nitrogen in the coke is a function of the constant C , which decreases with increasing temperature of carbonization, and of the yield of coke, which also decreases with increasing carbonization temperature. The above equation directly confirms the older statements in the literature to the effect that coals of high rank, which give high yields of coke, will give low yields of volatile nitrogen, and low-rank coals, which give low yields of coke, will give high yields of volatile nitrogen; that is, the amount of volatile nitrogen varies inversely with the rank of the coal.

The following equations were also derived for calculating the yield of ammonium sulfate obtainable from the various coals at various temperatures:

$$A = a + bN_V + c\bar{V}$$

where A = yield of ammonium sulfate in pounds per ton of coal charged.

a , b , and c = constants.

W = percentage of moisture in the coal.

It was found that the experimentally determined values for the nitrogen in the coke could not be used in calculating the ammonium sulfate yields because, if they were, the correlation coefficients were very low, whereas if the calculated values for the coke-nitrogen contents were used these coefficients were quite high. This is another

independent indication that the values obtained for the nitrogen content of coke samples either by the Kjeldahl or Dumas methods may be seriously in error.

It was found necessary to use the factor cW in calculating the yield of ammonium sulfate since, as is known, the moisture present in the coal has a definite protective influence against the decomposition of ammonia. A high moisture content is associated with coals of low rank so the necessity of using the factor cW may be attributed to the fact that low-rank coals give higher yields of ammonia than high-rank coals. The yield of ammonium sulfate as a function of temperature is shown in Table XIV. It is observed that the yield of

TABLE XIV

YIELD OF AMMONIUM SULFATE AS A FUNCTION OF TEMPERATURE ⁵⁰

Temperature	Number of Coals and Coal Blends Studied	Average Yield of Ammonium Sulfate
°C		pounds per ton of coal
500	50	4.3
600	52	10.8
700	51	21.7
800	54	22.0
900	88	19.5
1,000	53	14.4
1,100	30	11.7

ammonium sulfate reaches a maximum when the coal is carbonized at 800° C. These coals were carbonized in iron retorts, and it is known that iron is a catalyst for the decomposition of ammonia. Hence, it might be expected that if the coals had been carbonized in a refractory retort the maximum yield of ammonium sulfate might have occurred at a higher temperature. The yield of ammonium sulfate is dependent on the nitrogen content and the mois-

ture content of the coal as well as on the temperature of carbonization.

The yields of low-temperature tar bases as a function of the carbonizing temperature of British coals are given in Table XV.⁵¹

TABLE XV

YIELD OF TAR BASES AS A FUNCTION OF TEMPERATURE⁵¹

Temperature °C	Tar Yield, Percentage by Weight of Coal	Tar Bases, Percentage by Weight of Tar
400	3.9	1.62
450	5.62	2.06
500	7.06	2.35
550	8.00	2.66
600	7.60	3.00
650	6.90	3.15
700	6.24	2.54

The following primary and tertiary amines have been isolated from low-temperature tar: aniline, 2-methyl-, 2,4-dimethyl-, 2,4,6-trimethylpyridine, quinoline, and 2-methylquinoline.⁵² Aniline, pyridine, and 2-methylpyridine have been isolated from the aqueous liquor from low-temperature tar.⁵³ Low-temperature aqueous liquor has been found to contain 0.082 gram of bases and 0.397 gram of ammonia per liter.⁵⁴ The following bases were isolated from a low-temperature tar: aniline, toluidine, 2,4-, 2,5-, and 2,6-dimethylpyridine, 2,3,4-, 2,3,5-, 2,3,6-, and 2,4,6-tri-

methylpyridine, and three tetramethylpyridines.⁵⁵

In further work on low-temperature tar bases, in which temperatures above 120° C were avoided during the working up of the bases, the following compounds were isolated: aniline, pyridine, 2-methylpyridine, 2,4- and 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, quinoline, and 2-methylquinoline, plus a group of basic amorphous substances which were classified under the name of resinamines. In the aqueous liquors from the tar were also isolated aniline, pyridine, and 2-methylpyridine.⁵⁶ The following compounds were obtained from the gasoline fraction of a Zhurinsk primary tar: aniline, pyridine, 2- and 4-methylpyridine, and 2,4- and 2,6-dimethylpyridine. From the kerosene fraction was isolated a methylquinoline. Hydrogenation of a 265–325° C fraction of bases yielded primary amines, *n*-methylaniline, and *n*-dimethylaniline, but no hydrogenated tertiary bases.⁵⁷ Peat generator gas tar was found to contain 2.5 percent of nitrogen-containing bases extractable with sulfuric acid. The following were identified: aniline, pyridine, 2,3- and 2,5-dimethyl-, 2,3,5-trimethyl-, 1,2,3,4-tetramethyl-, 4-methyl 2-ethyl-, 3-ethyl-, and 3-isopropylpyridine, quinoline, isoquinoline, methyl- and dimethylquinoline, benzylquinoline, carbazole, acridine, methylacridine, and skatole.⁵⁸

As seen above, most of the bases isolated

⁵¹ Sinnatt, F. S., King, J. G., and Linnell, W. H., *J. Soc. Chem. Ind.*, **45**, 385–93T (1926).

⁵² Morgan, G. T., *J. Soc. Chem. Ind.*, **47**, 131–33T (1928).

⁵³ Morgan, G. T., and Pettet, A. E. J., *J. Soc. Chem. Ind.*, **56**, 109–14T (1937); Morgan, G. T., Pratt, D. D., and Pettet, A. E. J., *ibid.*, **48**, 89–93T (1929).

⁵⁴ Brown, R. L., and Branting, B. F., *Ind. Eng. Chem.*, **20**, 392–6 (1928).

⁵⁵ Komatsu, S., and Mohri, A., *J. Chem. Soc. Japan*, **52**, 722–6 (1931); *Chem. Abs.*, **26**, 4936 (1932).

⁵⁶ Morgan, G. T., *J. Soc. Chem. Ind.*, **51**, 67–80T (1932).

⁵⁷ Rapoport, I. B., and Kosolapov, Z. E., *Khim. Tverdogo Topliva*, **4**, 323–32 (1933); *Chem. Abs.*, **28**, 6280 (1934); *Khim. Tverdogo Topliva*, **5**, 448–55 (1934); *Chem. Abs.*, **29**, 7050 (1935).

⁵⁸ Kashtanov, L. I., Bulochnikov, M. V., and Zlotnikova, O. L., *J. Applied Chem. (U.S.S.R.)*, **9**, 737–41 (1936); *Chem. Abs.*, **30**, 7821 (1936).

from low-temperature tar are pyridine and quinoline derivatives. Four and one-half percent of the bases found in a primary tar were primary amines, and 2,4,6-trimethylpyridine was also isolated.⁵⁹ Other investigators⁶⁰ have failed to find primary amines in low-temperature tar, the tars containing: (1) 56 percent secondary, 44 percent tertiary amines (with traces of primary amines, pyridine, methylpyridine, diethylamine, and triethylamine in the aqueous liquor);^{60a} (2) 20 percent secondary and 80 percent tertiary bases;^{60b} (3) 15 percent secondary and 85 percent tertiary bases,^{60c} respectively, as reported by the above-mentioned authors. Secondary amines were found to predominate in a low-temperature tar with primary amines apparently absent.⁶¹ Pyridine, 2-methyl-, 2,4-dimethyl-, 3,4-dimethyl-, 2,4,6-trimethylpyridine, quinoline, and 2-methylquinoline have been isolated from primary tar.⁶² The presence of acetonitrile has also been reported in the same material.⁶³ In a low-temperature light oil 0.045 and 0.9 percent, respectively, of aniline and pyridine bases were found which correspond to 0.0004 and 0.009 percent, respectively, based on the coal.

The yield of ammonia obtained from commercial low-temperature coking varies greatly with the nitrogen content and the

manner of its linkage in the coal, the temperature used, the manner and rate of heating, and the time-temperature path of the tar vapors from their origin to their escape from the retort. The low-temperature distillation of bituminous coal at 500° C has been reported to yield 20 kilograms of ammonium sulfate per 1,000 kilograms of coal, which is a higher yield than is obtained from high-temperature coking.⁶⁴ Most authors, however, give figures of about 6 to 7 kilograms of ammonium sulfate per ton of coal.⁶⁵ The low-temperature distillation of brown coal and peat for recovery of ammonia is not practicable owing to the high water content of these fuels which causes the ammonia to be present in very dilute solutions (0.03 to 0.07 percent ammonia).

HIGH-TEMPERATURE DISTILLATION

High-temperature distillation products are characterized by their high aromatic content. Unrefined high-temperature light oil contains 1 to 3 percent of nitrogen bases consisting principally of pyridine and its derivatives with small quantities of aniline and pyrrole and 0.2 to 0.3 percent of nitriles (aceto- and benzonitrile).⁶⁶ The quantity of nitrogen bases obtained in the distillation of American coals over the temperature range of 500–1,100° C does not vary appreciably.⁴⁹ A 2.3 percent yield of tar bases (mainly pyridine, methylpyridines and dimethylpyridines, quinolines, and acridine) plus a 2.3 percent yield of carbazole and similar compounds have been reported from coke-oven tar.⁶⁷ 2-, 3-, 4-, 5-,

⁵⁹ Gollmer, W., *Brennstoff-Chem.*, **4**, 1–9, 19–24 (1923).

⁶⁰ (a) Brittain, A., Rowe, F. M., and Sinnatt, F. S., *Fuel*, **4**, 263–9, 299–307, 337–40 (1925). (b) Morgan, J. J., and Soule, R. P., *Chem. Met. Eng.*, **26**, 923–8, 977–81, 1025–30 (1922). (c) Parrish, E., and Rowe, F. M., *J. Soc. Chem. Ind.*, **45**, 99–106T (1926).

⁶¹ Edwards, K. B., *J. Soc. Chem. Ind.*, **43**, 143–56T (1924).

⁶² Schütz, F., Buschmann, W., and Wissebach, H., *Ber.*, **56**, 162–9, 869–74, 1967–75 (1923), **57**, 421–23 (1924).

⁶³ Schütz, F., and Buschmann, W., *Stahl u. Eisen*, **45**, 1232–42 (1925).

⁶⁴ Tremus, G., *J. Gasbeleucht.*, **63**, 397–S (1920).

⁶⁵ Thau, A., *Glückauf*, **61**, 6S2 (1925); *Brennstoff-Chem.*, **6**, 324 (1925).

⁶⁶ Lunge, G., *Coal Tar and Ammonia*, D. Van Nostrand, New York, 5th ed., 1916, part 2, p. 855.

⁶⁷ Weiss, J. M., and Downs, C. R., *Ind. Eng. Chem.*, **15**, 1022–3 (1923).

and 7-methylindoles have been isolated from coal tar.⁶⁸ In certain coal-tar oils boiling around 300° C, containing about 6 percent of tar bases, these bases were found to consist mainly of quinoline and isoquinoline derivatives of unknown structure plus a small quantity of primary amines from which were isolated α - and β -naphthylamines. The crude-tar base, b.p. 290–296° C, contained 8 to 10 percent of these two amines as judged from acetylation experiments.⁶⁹ 2,3-Benzocarbazole has been isolated from medium-soft tar pitch;⁷⁰ this compound had previously been obtained from coal tar.⁷¹ The bases from anthracene oil (b.p. 270–350° C) have been fractionally distilled, but a separation into pure compounds was unsuccessful.⁷² By chromic acid oxidation of the bases (b.p. 180–200° C_{30 mm.}) to form acids followed by preparation of phenylphenacyl esters, derivatives were obtained which indicated the presence of a dialkylquinoline or isoquinoline compound. From the fraction of b.p. 100–110° C_{2 mm.}, six picrates were obtained of m.p. 201, 181, 212, 230, 203, and 198° C. The first two picrates belonged to the series C₁₀H₉N, and the last four to the series C₁₁H₁₁N. The picrate of m.p. 198° C corresponded to that of 5,8-dimethylquinoline; the other bases appear to be new, although the 230° C picrate is possibly identical with 2,3-dimethylquinoline picrate isolated by Bailey from petroleum, which was found to melt at 231° C. The 230 and 201° C melting picrates have the same melting points as 4,6-dimethyl and 8-methylquinoline, respectively, but mixed melting points

with authentic samples showed depressions. The picrates of melting point 181° and 201° C are possibly those of 5- and 7-methylisoquinoline.

The bases from a pitch distillate were fractionally distilled and several amines isolated, among which were identified o-toluidine and β -naphthylamine. One of the higher-boiling amines was considered to be a highly condensed heterocyclic nitrogen compound corresponding to pyrene.⁷³ Carbazole, acridine, and a benzocarbazole have been found in a bituminous coal-tar pitch distillate (boiling range 230–435° C).⁷⁴

Nearly all the nitrogen-containing constituents of high-temperature coal tar are basic and form water-soluble salts with mineral acids. Some of these compounds are weak bases (pyrrole, indole, carbazole, benzocarbazole), and their salts are easily hydrolyzed; the majority of them have heterocyclic nitrogen atoms. The coal-tar bases boiling to 280° C may represent less than 0.5 percent by volume of the total tar. Distillation concentrates the bases, however, so that as much as 4 percent of mixed bases may be present in the tar oils

TABLE XVI

TYPICAL COAL-TAR BASES ⁷⁵

Boiling Range °C	Name	Percent
	Pyridine	7
124–145	Picolines	10
145–170	Lutidines	7
170–180	Collidines	3
180–230	30
230–240	Quinolines	24
240–280		19

⁶⁸ Kruber, O., *Ber.*, **59B**, 2752–60 (1926), **62B**, 2877–80 (1929).

⁶⁹ Kruber, O., *Ber.*, **66B**, 1653–4 (1933).

⁷⁰ Cook, J. W., Hewett, C. L., and Hieger, I., *J. Chem. Soc.*, **1933**, 395–8.

⁷¹ Grübe, C., and Knecht, W., *Ber.*, **12**, 341–3, 2242–3 (1879); *Ann.*, **202**, 1–19 (1880).

⁷² Ganguli, S. K., and Guha, P. C., *J. Indian Chem. Soc.*, **11**, 197–206 (1934).

⁷³ Hofmann, F., and Boente, L., *Brennstoff-Chem.*, **14**, 381–2 (1933).

⁷⁴ Zerbe, C., and Eckert, F., *ibid.*, **14**, 1–3 (1933), **15**, 28–31 (1934).

⁷⁵ Wilson, P. J., Jr., and Wells, J. H., *Ind. Eng. Chem., News Ed.*, **14**, 487–8 (1936).

TABLE XVII

NITROGEN BASES ISOLATED FROM HIGH-TEMPERATURE COAL TAR ⁷⁶

Name	Boiling Point °C	Melting Point °C
Pytrole	131	...
Pyridine	115	-42
Aniline	184	-8
2-Methylpyridine	129	...
3-Methylpyridine	143	...
4-Methylpyridine	145	...
<i>o</i> -Toluidine	200	-16
2,3-Dimethylpyridine	164	...
2,4-Dimethylpyridine	157	...
2,5-Dimethylpyridine	163	...
2,6-Dimethylpyridine	143	...
3,4-Dimethylpyridine	164	...
Indole	253	52.5
Dimethylaniline	193	2.5
Trimethylpyridine	165-8	...
2,4,5-Trimethylpyridine	167	...
2,4,6-Trimethylpyridine	171	...
2-Methylindole	271	61
3-Methylindole	265	95
4-Methylindole	267	5
5-Methylindole	267	60
7-Methylindole	266	85
Tetramethylpyridine
1,2,3,4-Tetramethylpyridine	233	...
Quinoline	238	-23
Isoquinoline	242	24
2-Methylquinoline	247	...
3-Methylquinoline	260	16
4-Methylquinoline	264	10
5-Methylquinoline	263	19
6-Methylquinoline	259	...
7-Methylquinoline	258	39
8-Methylquinoline	248	...
1-Methylisoquinoline	255	10
3-Methylisoquinoline	252	65
1-Naphthylamine	301	50
2-Naphthylamine	306	112
Dimethylquinoline
1,3-Dimethylisoquinoline	262	30
2,8-Dimethylquinoline	255	23
5,8-Dimethylquinoline	100-102 mm	...
Carbazole	352	245
Acridine	346	110
Phenanthridine	349	106
Hydroacridine	300 (dec.)	169
2-Methylcarbazole	363	259
3-Methylcarbazole	365	207
Benzocarbazole	450	340

boiling to 280° C. The proportions of some of the principal bases are shown in Table XVI.⁷⁵

Table XVII lists the amines and heterocyclic nitrogen compounds which have been isolated from high-temperature coal tar.⁷⁶

The nonbasic nitrogen compounds isolated from high-temperature coal tar are listed in Table XVIII.

TABLE XVIII

NONBASIC NITROGEN COMPOUNDS ISOLATED FROM HIGH-TEMPERATURE COAL TAR ⁷⁶

Name	Boiling Point °C	Melting Point °C
Acetonitrile	79	-41
Benzonitrile	196	-13
1-Naphthonitrile	297	34
2-Naphthonitrile	304	67

The formation of ammonia in high-temperature distillation of coal also greatly depends on the nitrogen content of the fuel, the retort temperature, the presence of moisture and other inert gases, the time-temperature path of the gases, and the velocity of heating. The amount of ammonia formed in high-temperature coking varies from 8.0 to 13.0 kilograms of ammonium sulfate per ton of coal. More ammonia is obtained when the coal is heated slowly (as in a coke oven in contrast to a gas retort). In the coke oven the moisture, slowly evolved from the coal, reacts with the glowing coke and converts some of the coke nitrogen into ammonia.

The division of nitrogen among the products obtained from high-temperature coking is given in Table XIX.

The division of nitrogen among the products of high-temperature distillation also depends on the geological age of the coal,

⁷⁶ Fisher, C. H., *U. S. Bur. Mines, Bull.* **412**, 31-2 (1938).

THE OCCURRENCE OF NITROGEN IN COAL

TABLE XIX

DIVISION OF NITROGEN AMONG HIGH-TEMPERATURE COKING PRODUCTS

Coals	Nitrogen Content					
	Coal percent	Coke percent	Tar percent	HCN percent	NH ₃ percent	Gas (Loss) percent
Westphalian I ⁷⁷	1.55	30.00	1.3	1.8	11.8	55.0
Westphalian II ⁷⁷	1.48	35.6	1.4	1.8	14.1	47.1
Westphalian III ⁸⁰	1.48-1.61	31-36	1.0-1.3	1.5-2.0	10-14	46-56
Saar ⁷⁷	1.18	63.9	4.1		15.9	16.1
English I ⁷⁸	1.73	48.68	...	1.56	14.50	35.26
English II ⁷⁹	1.57	43.31	2.98	1.43	15.16	37.12
English IV ⁸¹	1.43	58.3	3.9	1.2	17.1	19.5

TABLE XX

EFFECT OF AGE OF FUEL ON DISTRIBUTION OF NITROGEN IN HIGH-TEMPERATURE DISTILLATION PRODUCTS ⁸²

	Bituminous Coals from						Bohemian	
	West-phalia	Saar	Saxony	Silesia	Eng-land	Bohe-mia	Leaf	Brown
Nitrogen in coal	1.50	1.06	1.20	1.37	1.45	1.36	1.49	0.52
Percent of total nitrogen in coke	80	57	64	70	72	69	44	38
Percent of nitrogen volatilized	20	43	36	30	28	31	56	62

that is, upon the chemical structure of the nitrogen compounds present. The older coals require a higher temperature for maximum evolution of ammonia and more nitrogen remains in the coke; the nitrogen compounds of the older coals are more thermally stable. This is illustrated in Tables XX ⁸² and XXI. ⁸³

Older coals, having a smaller oxygen content than younger coals, are thus able to form less water during thermal decomposition and hence less steam is available to

TABLE XXI

EFFECT OF AGE OF FUEL ON DISTRIBUTION OF NITROGEN IN HIGH-TEMPERATURE DISTILLATION PRODUCTS ⁸³

	Peat (Bremen)	Gas Coal (York-shire)	Gas Coal (Consoli-dation)	Fat Coal (Aachen)	Anthra-cite (Aachen)
Coke yield	31.74	64.48	68.57	77.32	94.80
Percent of total nitrogen in coke	24.02	42.63		54.0	63.64
Percent of total nitrogen in ammonia	40.28	29.45	29.07	33.78	25.85
Percent of total nitrogen otherwise volatilized	35.70	27.92	27.33	12.19	10.51

protect the ammonia from decomposition into elementary nitrogen. ⁸⁴ At temperatures above 300° C, the organic nitrogen compounds in the coal are decomposed,

⁷⁷ Knublauch, *J. Gasbeleucht.*, **38**, 753-57, 769-73 (1895).

⁷⁸ Foster, W., *J. Gas Lighting*, **40**, 1081-2, 1124-6 (1882); *J. Chem. Soc.*, **43**, 105-10 (1883).

⁷⁹ Short, A., *J. Soc. Chem. Ind.*, **26**, 581 (1907).
⁸⁰ Knublauch, *J. Gasbeleucht.*, **26**, 440-48 (1883).

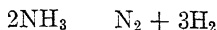
⁸¹ McLeod, J., *J. Soc. Chem. Ind.*, **26**, 137-9 (1907).

⁸² Heckel, W., *Stahl u. Eisen*, **33**, 402-5 (1913).

⁸³ Christie, M. G., *ibid.*, **30**, 1243 (1910).

O., *ibid.*, **30**, 1243 (1910).

forming ammonia; ammonia is also formed by the action of steam on the nitrogen in the coke, as in the Mond process.⁸⁵ The presence of gases such as nitrogen inhibits the thermal decomposition of ammonia into its equilibrium products:



However, for all practical coal coking purposes the above reaction may be considered to be irreversible, that is, proceeding only in the direction of ammonia decomposition. Steam also seems to have a specific protective action against the thermal decomposition of ammonia, because it exerts this protection when it is present in such small amounts that the mere dilution of the ammonia is negligible. This may be due to the formation of ammonium hydroxide.⁸⁶ Steam is preferentially adsorbed on iron surfaces; it has been suggested that this fact best explains the protective action of steam on the thermal decomposition of ammonia. Hydrogen chloride and other volatile acids as well as hydrogen sulfide also exert a protective action on the ammonia, whereas the presence of oxygen favors the decomposition of ammonia.

In a study of the linkage of nitrogen in coal Terres⁸⁷ postulated that, during the heating of coal, all the nitrogen which is evolved leaves the coal in the form of ammonia and that the other volatile nitrogen-containing compounds which ultimately appear, such as elementary nitrogen, cyanogen, and hydrogen cyanide, are formed as

the result of secondary reactions. To find out what types of nitrogen linkages will actually yield ammonia on dry distillation, organic compounds containing amino, substituted amino, azo, hydrazo, isonitrile, and nitro groups were pyrolyzed. The compounds actually used were: glycine, asparagine, albumin, animal gelatin, pyridine, azobenzene, acetonitrile, phenylisocyanate, hydrazobenzene, and nitrobenzene. It was found that only compounds containing amino or substituted amino groups yielded ammonia on pyrolysis, and it was concluded that the nitrogen in coal must be held in this type of linkage.

However, it must be remembered, in dealing with coal, that a high-molecular-weight, low-volatile substance is involved and, on heating, the primary decomposition process may yield a variety of compounds which contain amino or substituted amino groups although the nitrogen in the coal may have originally been linked in some quite different fashion. At least there is no direct experimental evidence to indicate that amino or substituted amino groups are present, as such, in coal. It is possible to detect amino groups in peat and in humic acids by the carbylamine test, but it is not possible to detect such groups in any of the higher-rank fuels.⁸⁸ Furthermore, from evidence obtained in a study of petroleum bases,⁴² it is found that basic heterocyclic nitrogen compounds are formed on mere distillation of petroleum, although such basic compounds are not present, in a free state, in the original material.

The behavior of coal nitrogen during pyrolysis has been studied by heating a Saxony bituminous coal in a platinum crucible for 7 minutes at various temperatures and determining the nitrogen remaining in

⁸⁵ Eastwood, A. H., and Cobb, J. W., *Gas World*, **93**, 597-9 (1930); *Brennstoff-Chem.*, **12**, 91 (1931).

⁸⁶ Trenkler, H. R., cf. Gluud, W., *Handbuch der Kokerei*, Wilhelm Knapp, 1927, Halle, Vol. I, p. 85; see also Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coking Industry*, Chemical Catalog Co., New York, 1932.

⁸⁷ Terres, E., *J. Gasbeleucht.*, **59**, 519-21 (1916).

⁸⁸ Christie, M. G., dissertation, Aachen, 1908.

the coke.⁸⁹ The results are shown in Table XXII. In considering these figures the uncertainty of the determination of nitrogen in coke should be kept in mind; this uncertainty probably explains the irregularities in the series.

TABLE XXII

EFFECT OF TEMPERATURE ON NITROGEN REMAINING IN COKE⁸⁹

Temperature of Crucible	Nitrogen Remaining in Coke (Dry, Ash-Free) percent
Original coal	1.71
500-520	1.49
520-530	1.17
550-560	1.49
600-620	1.31
650-670	1.26
700-710	1.39
750-770	1.19
800-820	1.02
850-875	1.41
900-930	0.72
950-975	0.94
1,000-1,020	0.47

The division of nitrogen among the products formed during the distillation of peat at 500° C is essentially the same as that obtained in coking a bituminous coal at a much higher temperature.¹⁷ When peat was distilled at different temperatures the

TABLE XXIII

EFFECT OF TEMPERATURE ON DISTRIBUTION OF NITROGEN IN PEAT DISTILLATION PRODUCTS¹⁷

	High Moor		Low Moor	
	450° C	550° C	800° C	650° C
	percent	percent	percent	percent
Total nitrogen in tar	0.56	0.65	0.86	3.24
Total nitrogen appearing as free bases	11.0	10.0	10.6	17.8
Bound bases	3.0	3.9	1.7	3.4

⁸⁹ Künle, O., *Brennstoff-Chem.*, **9**, 295-S (1928).

percentage of the total nitrogen of the tar found in the form of so-called free bases is shown in Table XXIII.

By direct extraction of the bases from the tar with warm sulfuric acid the ratio of basic to nonbasic nitrogen in the extract was that shown in Table XXIV. The

TABLE XXIV

RATIO OF BASIC TO NONBASIC NITROGEN IN PEAT TAR¹⁷

Tar °C	Free Bases from Nitrogen Balance percent	From Acid Extraction	
		Basic Nitrogen percent	Nonbasic Nitrogen percent
450	11	11	89
550	10	20	80
650	17.8	30	70
800	10.6	13	87

major part of the nitrogen in the tar is linked in the form of nonbasic nitrogen. The higher values for basic nitrogen obtained in the extraction experiments is explained as due to the inclusion of some of the bases present in the pitch-forming constituents ("bound bases").

The relative amounts of primary, secondary, and tertiary bases in the peat tar were also determined and are given in Table XXV. Table XXV shows that the tertiary bases strongly predominate in the tar. The isolation of pure individual compounds from the various fractions was at-

TABLE XXV

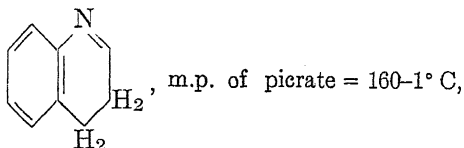
RATIO OF PRIMARY, SECONDARY, AND TERTIARY BASES IN PEAT TAR¹⁷

	Peat Tar Prepared at				
	450 * °C	550 * °C	650 * °C	650 † °C	800 * °C
Tertiary bases, percent	83.8	88.4	87.3	89.9	86.3
Secondary bases, percent	10.6	8.8	6.7	5.0	6.4
Primary bases, percent	0.8	1.7	1.3	1.2	2.8

* Nitrous acid method.

† Benzenesulfonechloride method.

tempted but failed with the exception that one compound, probably dihydroquinoline,



was isolated from the 250–5° C fraction of the bases from the 650° C tar.

The majority of the bases which have been isolated from both low- and high-temperature distillation of solid fuels are identical. Low-temperature distillation, therefore, represents a sufficiently severe thermal treatment to convert the nitrogen-containing compounds present in solid fuels largely into purely aromatic type bases such as pyridines, quinolines, etc., although there is evidence to the effect that considerable amounts of secondary amines are present in low-temperature tar. This may mean that hydroaromatic bases are also present such as were found in the products resulting from solvent extraction and from vacuum distillation.

GASIFICATION

Gasification of coals and peat by incomplete combustion with air or steam, or both, volatilizes all the nitrogen from both the coal and its coke. The form in which the nitrogen finally appears depends on the manner of gasification. The gasification process is preceded by low-temperature and then high-temperature coking, these processes being brought about by the hot gases produced by the combustion of the coal in the lower levels of the generator. The fate of the nitrogen-containing compounds then depends on the velocity of gasification, the amount of steam present, the amount of air blown through the charge, and the temperature. If no steam is present no ammonia results and all the

nitrogen in the coal appears as elementary nitrogen just as in combustion. By addition of steam during the gasification, nearly theoretical yields of ammonia can be obtained (Mond process). Gasification yields very little information about the type of nitrogen linkages in coal.

COMBUSTION

In the combustion of solid fuels all the nitrogen is volatilized and appears in the combustion products as elementary nitrogen, oxides of nitrogen, etc. A direct simultaneous method for the microdetermination of carbon, hydrogen, and oxygen in solid fuels, based on combustion, has been developed.⁹⁰ Before being applied to solid fuels the method was first tried with pure organic compounds containing a variety of nitrogen linkages.⁹¹ It was found that compounds containing heterocyclic nitrogen, nitrile and nitro groups, or amino and amide groups, when subjected to complete combustion in oxygen, fell into two distinct groups so far as the amount of "oxygen consumed" during their combustion is concerned. When bituminous coals were subjected to combustion by the same method it was found that much more reasonable results were obtained for their oxygen contents when it was assumed that the nitrogen in the coal is bound in a linkage of the first type rather than in the form of amino or amide groups. Among the linkages of the first type the heterocyclic nitrogen linkage seemed the most likely to be present in coal. When the same method was applied to a "nitro humic acid," the results confirmed the suggestion⁹² that the nitrogen, added to coal on treatment with nitric acid, is present in the form of an isonitroso

⁹⁰ Kirner, W. R., *Ind. Eng. Chem., Anal. Ed.*, **8**, 57–61 (1936).

⁹¹ Kirner, W. R., *ibid.*, **7**, 366–8 (1935).

⁹² See pp. 201–2 of ref. 4.

ketone linkage. With coke the best results were obtained on the assumption that all the nitrogen of the coke is finally present in the combustion products as elementary nitrogen.

OXIDATION

Very little attention seems to have been devoted to the fate of nitrogen in coal which has been subjected to oxidation. On benzene pressure Soxhlet extraction 100 grams of Estevan brown lignite (0.95 percent nitrogen, dry, ash-free) gave a residue, 95.5 grams (nitrogen content not reported), which, on partial alkaline permanganate oxidation, yielded "regenerated" humic acids, 57.2 grams, containing 1.2 percent nitrogen (dry basis).⁹³ This indicates that the nitrogen compounds present in the humic acids are resistant to oxidation. Humic acids, prepared by oxidation of coal with 1.0 N nitric acid, have considerable nitrogen introduced into the molecule. Thus, humic acids prepared in this way by oxidizing for approximately one week contain 2.73 to 4.05 percent nitrogen.⁹⁴ The nitrogen content of such products diminishes as the oxidation continues. (See Table XXVI.⁹⁵)

TABLE XXVI

EFFECT OF OXIDATION ON NITROGEN CONTENT OF OXIDIZED COAL ⁹⁵

	Nitrogen Content	
	5-Day Oxidation percent	52-Day Oxidation percent
Humic acids	9.2	0.8
Soluble acids	4.5	3.1

⁹³ Bone, W. A., Horton, L., and Ward, S. G., *Proc. Roy. Soc. (London)*, **127A**, 485, 504-5 (1930).

⁹⁴ Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **57**, 512-16 (1935).

⁹⁵ Juettner, B., Smith, R. C., and Howard, H. C., *ibid.*, **57**, 2322-6 (1935).

This behavior is explained as due to a part of the nitrogen in the humic acids being held in the form of isonitroso ketone groups,⁹² which are removed by hydrolysis during the later stages of the oxidation. However, the fact that some nitrogen is still retained even after 52 days of refluxing with the oxidation mixture indicates a resistant type of structure. More convincing evidence of the presence of nitrogen which is resistant to oxidation was obtained by oxidizing coal with gaseous oxygen in aqueous alkali at 225° C and 25 atmospheres.⁹⁶ No nitrogen could have been added by the reagents. The so-called aromatic acids thus obtained contained 0.45 percent nitrogen. On decarboxylation of these acids with aqueous alkali the odor of pyridine could be plainly detected.

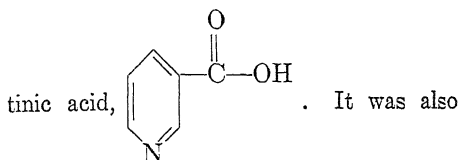
A clue to the probable type of such nitrogen has been found.⁹⁷ When nitrogen in coal is determined by the Kjeldahl method, if the digestion is stopped as soon as the sulfuric acid becomes clear, the values for nitrogen are always low. Beet Kjeldahlized 1,000 grams of a coal which contained 1.7 percent nitrogen; of the 17.0 grams of nitrogen present, 13.6 grams were accounted for as ammonia after digestion with sulfuric acid until a clear solution was obtained (72 hours). On working up the product to determine the source of the loss of 3.4 grams of nitrogen he obtained a dry product of which 9 grams was alcohol-soluble (containing 7.2 percent nitrogen) and 21 grams alcohol-insoluble (containing 2.4 percent nitrogen). These substances accounted for 1.15 grams or 33.8 percent of the loss.

From the alcohol-insoluble fraction were isolated crystalline silver salts which, on analysis for carbon, hydrogen, nitrogen, and

⁹⁶ Smith, R. C., Tomarelli, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **61**, 2398-2402 (1939).

⁹⁷ Beet, A. E., *Fuel*, **19**, 108-9 (1940).

silver, gave values between those theoretically required for pyridine mono- and dicarboxylic acid. Heating the silver salts with soda lime gave pyridine and ammonia. From the alcohol-soluble portion was isolated a silver salt which analyzed reasonably closely to that of a pyridine monocarboxylic acid. X-ray spectrograms indicated that the silver salt was that of nicotinic acid,



found that 240 hours' digestion of nicotinic acid with sulfuric acid was necessary to convert all its nitrogen into ammonia. Digestion for shorter periods gave pyridine along with ammonia. The addition of catalysts, e.g., potassium sulfate, mercuric oxide, and selenium, materially shortens the time necessary to convert all the nitrogen to ammonia, but only with potassium sulfate and selenium was no pyridine formation observed.

When humic acids are oxidized with fuming sulfuric acid, the nitrogen present in the original material is practically quantitatively recovered in the oxidized humic acids.⁹⁸ It therefore appears that the nitrogen in the original humic acids is very firmly fixed in the carbon nucleus, possibly in heterocyclic rings.

HYDROGENATION

Coals of various ranks have been hydrogenated with phosphorus and hydriodic acid under pressure and at temperatures from 200 to 280° C.⁹⁹ It was found that

hydrogenation was easiest and proceeded farthest with young coals, as based on the amount of material extractable with chloroform. With a gas flame coal, the youngest of the bituminous coals, it was found that the hydrogenation product was completely nitrogen free whereas the hydriodic acid solution contained considerable quantities of ammonia and organic amines.

A Lower Silesian coal, in the form of dust, was hydrogenated, the crude oil obtained was distilled, and the bases present in the various fractions were extracted; they amounted to 3.8 percent of the crude oil.¹⁰⁰ Preliminary experiments indicated the presence of primary bases but no pyrolyse derivatives. The bases were diazotized, and the nitrosoamines and phenols formed from the diazonium salts were separated from the tertiary amine salts by extraction with ether. The phenols which were isolated indicated the presence of aniline, toluidines, and xylydines. No products could be identified among the nitrosoamines, owing to their resinification. Pyridine was found to be absent in the tertiary base fraction. The following substances were definitely identified: 2,4,6-trimethylpyridine, quinoline, 2-methylquinoline, and isoquinoline; three additional unidentified bases were also isolated.

A brown coal semicoke was also hydrogenated and a cursory study made of the bases present in the tar.¹⁰¹ A fraction of boiling point 180–200° C consisted of primary bases to the extent of 33 percent.

An Eocene brown coal, containing 1.04 percent nitrogen, was hydrogenated under 110 atmospheres, cold pressure, and 470° C, and the manner in which the nitrogen was distributed in the products was investi-

⁹⁸ Pearson, A. R., *J. Soc. Chem. Ind.*, **42**, 68-72T (1923).

⁹⁹ Fischer, F., and Tropsch, H., *Ges. Abhandl. Kenntnis Kohle*, **2**, 154-9 (1917).

¹⁰⁰ Heyn, M., and Dunkel, M., *Brennstoff-Chem.*, **7**, 20-25, 51-7, 245-50 (1926).

¹⁰¹ Tropsch, H., and Ter-Nedden, W., *Brennstoff-Chem.*, **6**, 143-5 (1925).

gated.¹⁰² (See Table XXVII.) Since, on dry distillation of this coal, only 12 to 20 percent of the coal nitrogen was converted into ammonia, it is apparent that hydrogenation yields considerably larger amounts (41 percent). The nitrogen in the oil is mainly linked in the form of bases.

TABLE XXVII

DISTRIBUTION OF NITROGEN IN HYDROGENATED
BROWN COAL PRODUCTS¹⁰²

	Percent Nitrogen of Coal
In oil	31.4
In ammonia (in gas)	11.8
In ammonia (in water)	29.2
In residue	19.2
As nitrogen (N_2)	8.4

The bases present in brown coal benzene (boiling to 230° C), prepared as above, have also been studied.¹⁰³ This benzene contained 3 percent of bases, which were extracted with 10 percent sulfuric acid and distilled as follows: start of boiling, 160° C, 28 percent between 160 and 200° C, 20.5 percent between 200 and 260° C, and 51.5 percent distilled above 260° C. The bases were found to be about 80 percent tertiary bases.

It has been shown that the removal of nitrogen from coal by hydrogenation at 1,000 pounds per square inch (cold pressure) and at temperatures from 385 to 415° C is slow and approximately constant and that complete removal of the nitrogen would be difficult by this method.¹⁰⁴ At 415° C, a coal containing 1.7 percent nitrogen yielded a pitch still containing 1.1 percent nitrogen after 12 hours of hydrogenation. Since the removal of oxygen by

hydrogenation was very rapid during the first 3 hours and then sharply became much slower, it was considered probable that there are at least two types of oxygen linkages in the coal substance. The suggestion has been made that the easily removed oxygen is possibly of a linear ether type because of the consequent diminution in the molecular weight of the coal substance, while the difficultly removable oxygen probably corresponds to linkages of a different type, possibly heterocyclic ether linkages. By the same argument, the nitrogen in the coal would appear to be bound in a more or less uniform manner; that is, the linkages appear to be of a single type.

If the benzene pressure extract of a bituminous coal is fractionated into petroleum ether insoluble-ether soluble and petroleum ether insoluble-ether insoluble portions and the latter then hydrogenated over Adkins' catalyst at 100 atmospheres (cold pressure), practically all the nitrogen, as well as the oxygen and sulfur, are removed at a temperature of 425° C.¹⁰⁵ Biggs pictured the nitrogen atoms as being held in the coal molecule either in a heterocyclic ring or as a link between two carbocyclic nuclei, with a possible random distribution throughout the coal structure.

Hydrogenation is probably the most effective tool for the ultimate determination of the type of nitrogen linkages in coal, and it is suggested that future investigators who use hydrogenation methods on coal devote their attention to this interesting and as yet unsolved problem.

CHLORINATION

As a result of the exhaustive chlorination of a bituminous coal suspended in antimony pentachloride and treated with chlorine for 6 days at 200° C, it has been found that

¹⁰² Von Makray, I., *Brennstoff-Chem.*, **11**, 61-4 (1930).

¹⁰³ Varga, J., and von Makray, I., *Brennstoff-Chem.*, **12**, 21-2 (1931).

¹⁰⁴ Fisher, C. H., and Eisner, A., *Ind. Eng. Chem.*, **29**, 1371-6 (1937).

¹⁰⁵ Biggs, B. S., *J. Am. Chem. Soc.*, **58**, 484-7 (1936).

the nitrogen content of the nonvolatile chlorinated residue was 50 percent higher than that of the original coal.¹⁰⁶ This increase in nitrogen content could not be traced to the reagents used. It was suggested that chlorination altered the nature of the nitrogen bonds in the coal so that the nitrogen which had previously escaped determination by the Kjeldahl method now became readily converted into ammonia during Kjeldahlization. In support of this suggestion it was observed that the chlorinated residues were much more easily digested than the original coal samples.

Other investigators¹⁰⁷ also found that a considerable portion of the nitrogen present in coal was retained in the nonvolatile chlorinated products. This has been taken as an indication that the nitrogen in coal is in a highly stable form and is an integral part of the ring structure of the coal.

ACTION OF AQUEOUS ALKALI ON COAL

A bituminous coal was heated with various concentrations of aqueous sodium hydroxide solutions (from 1 *N* solution to 100 percent) under pressure and at various temperatures up to 400° C.¹⁰⁸ The residues remaining after this treatment in general had a higher nitrogen content than the original coal, indicating that the nitrogen became concentrated in the residues. The total nitrogen recoveries in some cases averaged over 100 percent, which was taken as an indication that here also the nitrogen in the residues had become more amenable to Kjeldahlization than in the original coal. The fact that the nitrogen content of the residues increased, coupled with the fact¹⁰⁹

that no appreciable odor of ammonia was observed on opening the bombs in which the reactions were carried out, certainly indicates that only insignificant amounts of the nitrogen in coal can be bound as amide linkages, for these would certainly be hydrolyzed under such drastic conditions. This agrees with the statement¹¹⁰ that the nitrogen compounds in coal split out only small amounts of ammonia when treated with aqueous alkali.¹¹¹

Evidence obtained concerning the linkage of nitrogen in coal as deduced from combustion, oxidation, hydrogenation, chlorination, and hydrolysis indicates that the nitrogen in coal is highly resistant to such processes. This type of resistance is best explained on the assumption that a large part of the nitrogen in coal is held in the form of heterocyclic linkages or as linear linkages between large complex carbocyclic groups.

THE NITROGEN IN COKE

Relatively little information is available concerning the linkage of nitrogen in coke. Ordinarily, coke prepared at high temperature contains 0.4 to 1.5 percent nitrogen which is held in an extremely heat-stable combination. The nitrogen-containing compounds in coal, on being rapidly superheated to temperatures above 750° C, undergo decomposition during which reactions occur between the nitrogen and carbon atoms forming thermally stable complexes which are represented as C_xN_y , and which are called "carbon nitrides."⁸⁸ At temperatures above 950° C, these compounds also begin to decompose with loss of elementary nitrogen as shown in Table XXVIII. The fact that treatment of coke

¹⁰⁶ Weiler, J. F., *J. Am. Chem. Soc.*, **58**, 1112-4 (1936).

¹⁰⁷ Heathcoat, F., and Wheeler, R. V., *J. Chem. Soc.*, **135**, 2839-47 (1932).

¹⁰⁸ Kasehagen, L., *Ind. Eng. Chem.*, **29**, 600-4 (1937).

¹⁰⁹ Kasehagen, L., private communication.

¹¹⁰ Strache, H., and Lant, R., *Kohlenchemie*, Akademische Verlagsgesellschaft, Leipzig, 1924, p. 283.

¹¹¹ See p. 79 of ref. 8a.

TABLE XXVIII

EFFECT OF TEMPERATURE ON LOSS OF NITROGEN FROM COKE¹¹²

Time of Heating hours	Temperature °C	Nitrogen in Coke		Loss in Nitrogen	Hourly Loss
		Before Heating percent	After Heating percent	Percent of Total Nitrogen	Percent of Total Nitrogen
12	850	1.58	1.61
15	950	1.76	1.41	15	1
34	1,350	1.67	0.35	56	2
7	1,450	1.32	0.48	63	9
2.5	1,500-1,900	1.67	0.21	87	25

with steam (the Mond process) results in nearly quantitative removal of the coke nitrogen as ammonia is in accord with the assumption that the nitrogen is bound to the coke in a manner similar to that in organic nitriles.

Another point of view represents the nitrogen in coke being held in the form of ring compounds.¹¹³ Since low-temperature coke contains a considerable amount of nitrogen and since such coke does not consist of elementary carbon but rather of a mixture of carbon-rich organic compounds, it is believed unlikely that the nitrogen in such compounds would be held in the form of "nitriles." However, since not all the nitrogen can be removed from coke by thermal treatment alone, regardless of how high a temperature is used, the nitrogen may possibly be held as nitriles in high-temperature coke.

More recently the results of an experimental study of the reactions of synthetic nitrogenous chars have been compared with those obtained on an essentially ash-free coke.¹¹³ A Ruhr gas coal containing 1.72 percent nitrogen was extracted with hot hydrochloric and hydrofluoric acids. The

ash content was reduced from 2.4 to 0.2 percent while the nitrogen content was not appreciably changed. This coal was coked at 1,000° C, and the resulting coke contained 0.3 percent ash and 1.7 percent nitrogen. The nitrogen content of the coke was independent of the ash content, and it was concluded that the nitrogen in the coke must be present in organic combination.

The synthetic nitrogenous chars shown in Table XXIX were prepared.¹¹³ The amount of nitrogen fixed depended on the properties of the char sample. The chars did not take up any nitrogen when heated in the presence of pure elementary nitrogen at high temperature. Crystalline forms of carbon, diamond and graphite, did not form nitrogenous chars when heated with ammonia at 700° C.

The behavior of the synthetic nitrogenous chars was studied by heating them in a current of nitrogen. Sample 8, when heated at 850° C, decomposed nearly quantitatively into a carbonaceous residue and cyanogen; the residue still contained about 7 percent of nitrogen. Sample 7, heated at 900° C, was quantitatively decomposed into cyanogen. Sample 9, heated at 900° C, slowly lost about 75 percent of its nitrogen as cyanogen, leaving a small amount of nitrogen in the residue. Sample 1, heated at 950° C, lost over half of its nitrogen but in the form of elementary nitrogen and not as cyanogen. The same was true for sample 6 except that about 20 percent of the nitrogen appeared as cyanogen, 45 percent as elementary nitrogen, and 35 percent remained in the residue. When the ash-free coke, prepared from coal, was heated at 950° C, it slowly lost elementary nitrogen but with no appearance of cyanogen.

Similarly, when these substances were heated in a vacuum, sample 7 was decomposed to the extent of 60 percent at 750° C. Sample 8 began to decompose at 525° C;

¹¹² See p. 410 of ref. 110.

¹¹³ Wibaut, J. P., *Proc. Intern. Conf. Bituminous Coal, 3rd Conf.*, 1, 665-73 (1931). Van der Ley, P. H., and Wibaut, J. P., *Rec. trav. chim.*, 51, 1143-56 (1932).

TABLE XXIX

SYNTHETIC NITROGENOUS CHARS¹¹³

Sample	Sugar Char		Activated Sugar Char		Supra Norit		Para Cyanogen	$(C_3N_2)_x^*$	$(C_4HN)_x^\dagger$
	Treated with		Treated with		Treated with				
	NH_3	$(CN)_2$	NH_3	$(CN)_2$	NH_3	$(CN)_2$	$(CN)_x$		
	1	2	3	4	5	6	7	8	9
Temperature of maximum nitrogen fixation, °C	700	700	700	800	800	800	500	430	450
Percent nitrogen in chars	1.3	2.2	2.5	7.5	3.1	10.6	53.7	40.5	19.4

* Prepared from tetraiodimidazole.

† Prepared from tetraiodopyrrole.

when it was heated at 860° C for 2 hours, 92 percent of the nitrogen was split off and the carbonaceous residue contained about 10 percent of nitrogen. On the other hand, the ash-free coke did not begin to decompose until 800° C was reached and its decomposition rate was much slower. Heating at 1,000° C for 10 hours reduced its nitrogen content from 1.8 to 0.4 percent.

It was thus found that samples 7, 8, and 9 were decomposed thermally at much lower temperatures than the nitrogen-carbon complex present in the ash-free coke. During thermal decomposition of the nitrogen-rich polymers most of the nitrogen was split off as cyanogen, whereas no trace of cyanogen was produced during the decomposition of the ash-free coke, the evolved nitrogen appearing entirely as elementary nitrogen. The nitrogenous chars, samples 1 and 6, on the other hand, behaved similarly to the ash-free coke.

The above compounds were also heated in a stream of hydrogen and the rate of ammonia formation was determined. A great difference in their reactivity with hydrogen was found. Nearly 50 percent of the nitrogen was converted to ammonia when sample 8 was heated at 500° C for 1

hour and 98 percent when it was heated at 700° C for 20 minutes. Sample 1 still contained about 70 percent of its nitrogen after being heated at 700° C for 1 hour, and sample 6 contained about 50 percent of its nitrogen after the same treatment. The ash-free coke, on the other hand, yielded scarcely any ammonia at 750° C, and the reaction was still slow at 1,100° C, only about 30 percent of its nitrogen being converted to ammonia in 5 hours.

From the above experiments it was concluded that the nitrogen in coke is bound chemically to carbon as a carbon-nitrogen complex, the nitrogen in coke showing properties analogous to the nitrogen in a nitrile group. This follows from the fact that both types of compounds yielded their nitrogen as ammonia when they were treated with steam or hydrogen at high temperature. The nitrogenous chars prepared from sugar char or activated carbon and ammonia showed the closest analogy to coke. The nitrogen could not be present as adsorbed nitrogen because it was converted to ammonia by the action of hydrogen at 600° C. The nitrogen in such compounds was regarded as being fixed to the unsaturated surface carbon atoms of the

char. A surface carbon, with three free valences, was believed to react with an ammonia molecule with the liberation of hydrogen, the nitrogen attaching itself to the carbon, forming a nitrile group. The more active the char the higher was the nitrogen content; crystalline modifications of carbon absorbed no nitrogen. Hence, the nitrogenous chars were regarded as surface compounds in which the nitrile groups were present on the surface. The nitrogenous chars prepared from cyanogen were considered to have both cyanogen groups and nitrogen atoms adsorbed on the surface. The cyanogen groups were removed as cyanogen during thermal treatment. Although samples 8 and 9 originally contained their nitrogen in the form of heterocyclic rings, these rings appeared to be thermally unstable and the nitrogen-containing carbonaceous residues which finally resulted were believed to be constituted similarly to the nitrogenous sugar chars, namely, the nitrogen to be held on the surface of the carbon in the form of a nitrile group.

SUMMARY

Nitrogen is present in all fossil fuels. On the basis of investigations of the origin of coal and of studies involving the extraction of low-rank fuels, it is concluded that the nitrogen is derived from plant or animal proteins, or both, as well as from plant alkaloids, chlorophyll, and similar porphyrins. Amino acids are formed by the hydrolysis of the proteins and can condense with carbohydrates, which are also

formed from plant materials, to form highly resistant nitrogen-containing complexes that permit the accumulation of nitrogen in the fossil fuel. Probably the types of nitrogen-containing organic compounds which can resist decomposition over geological periods of time would have their nitrogen atoms present in heterocyclic linkages or in complex molecules in which the nitrogen atoms are protected. Some evidence indicates that a large part of the nitrogen in humic acids is also bound cyclically.

By considering the results obtained from studies of solvent extraction, vacuum distillation, low- and high-temperature distillation, gasification, combustion (all of which represent progressively increasing severity of thermal treatment), oxidation, hydrogenation, halogenation, and hydrolysis of coals of various rank, the nitrogen in coal can be pictured as being present in a heterocyclic linkage in a molecule of high molecular weight. Such linkages are quite resistant to fission. As the rank of the coal increases, the amount of nonbasic nitrogen present also increases. On sufficiently vigorous thermal or chemical treatment of the higher-rank fuels, reactions occur which result in the formation of heterocyclic compounds of lower molecular weight; the basicity and aromaticity of these heterocyclic compounds increase with increasing severity of treatment.

The manner in which nitrogen is linked in coal appears to be markedly similar to the way in which it is linked in crude petroleum.

CHAPTER 14

COMPOSITION AND ORIGIN OF THE MINERAL MATTER IN COAL

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OCCURRENCE

That coal contains some other material than organic coal substance is apparent when the coal is examined in place in the bed, after being mined or finally prepared for market, and, finally, when the residue from its combustion is examined. In the bed this extraneous matter is apparent as definite horizontal layers of varying thickness and extent, as surface deposits or fillings in the vertical cleats, and more unusually as intrusions of claylike or other material irregularly through the coal.

The horizontal layers in the coal are usually shaley or pyritic in appearance and vary greatly in thickness, from thin streaks to layers of several inches or more; they may be limited and local in extent, or they may be very persistent over great areas, like the blue band of the No. 6 Seam of coal in Illinois. Bands of considerable thickness and extent may be considered to separate different coals, or to be merely one phase of a coal. In any event, such extensive bands are taken account of in mining the coal. Such bands have been formed when the coal-forming deposits were laid down.

The deposits in the shrinkage cracks or cleats which may, for example, be kaolinite, calcite, gypsum, or pyrite, are usually thin surface deposits and may not always be

present. They were obviously laid down later in the coal-forming process.

The larger adventitious bodies of foreign matter in the coal, referred to as clay veins, sandstone intrusions, washouts, and the like, are the result of rather unusual geological conditions during and after the time the coal was laid down.

Much of the mineral matter, and therefore the ash content, of prepared coal comes from the inclusion during mining of roof or floor rock, of the impure streaks, or of some of the larger impurities. Such inclusions may be deliberate in that no effort is made to remove them during the mining operation, or they may be accidental in that their elimination during mining was not complete. Such material may easily be removed by coal-cleaning methods. With the increasing use of mechanical methods of mining, and particularly in large-scale strip operations, it is becoming the practice to do little exclusion during mining and to subject the coal to a cleaning process during preparation.

Besides these large and obviously recognizable impurities in the coal, similar material may be distributed throughout it, usually irregularly in smaller aggregations.

Many of such inclusions are recognizable only with the aid of the microscope. The coarser make-up of the coal seam, including the occurrence of such adventitious

impurities, has been well described by Rais-trick and Marshall¹ and Stutzer and Noé.²

The smaller occurrences of mineral matter, and particularly of microscopic particles of mineral matter, have been well described by Sprunk and O'Donnell.³

Mineral matter in coal has frequently been classified as inherent and extraneous mineral matter. The inherent mineral matter is defined as that mineral matter which had its origin in the organic constituents of the plant giving rise to the coal bed;⁴ the extraneous, as that which was brought into the coal-forming deposit by mechanical means from outside, for example, as dust by air or as suspended or dissolved material carried by water. The inherent mineral matter is also sometimes defined as the inorganic material combined with the organic coal substance. Such material need not be derived from the coal-forming plants. The inherent mineral matter is generally very small in amount. The major portion of the mineral matter of commercial coal is extraneous or adventitious.

COMPOSITION

The ash content and chemical analysis of the ash from a sample of coal show the average content of inorganic elements in a coal but do not, of themselves, indicate the nature or distribution of the mineral matter in the coal. However, they do provide many valuable data which, used along with other information, can give a very good picture of the mineral content of the coal. Examinations of numerous coal-ash

analyses, calculated to a sulfur trioxide-free basis, show that, with few if any exceptions, over 95 percent of coal ash is composed of alumina, silica, iron oxide, lime, and magnesia, the magnesia content frequently being negligible. The remaining 5 percent includes such items as sodium oxide, potassium oxide, phosphorus pentoxide, chlorine, titanium oxide, and analytical errors. The values for these items making up the 5 percent become even less important when the ash analysis is calculated back to the original mineral matter in the coal because of the loss of water of hydration from the clay minerals, the loss of carbon dioxide by the carbonate minerals, and the replacement of two atoms of sulfur by one and one-half atoms of oxygen in the conversion of pyrite to ferric oxide. The minerals present in the coal must, therefore, have been composed of these substances.⁵

Furthermore, an examination of a large number of coal analyses shows that coal ashes contain silica, lime, alumina, and iron oxide in amounts within the following limits:

OXIDE	MAXIMUM	MINIMUM
SiO ₂	70	15
Al ₂ O ₃	40	0
CaO	55	0
Fe ₂ O ₃	60	0

It must be remembered that such ash analyses are analyses of ash compositions averaged over the entire coal. The analyses of ashes obtained from individual pieces of coal may vary widely even when the pieces are selected from closely adjacent places in the same seam.

Working from analyses of coal ashes, various investigators have attempted to calculate and reconstitute the kind and

¹ Raistrick, A., and Marshall, C. E., *Nature and Origin of Coal and Coal Seams*, The English University Press, London, 1939, pp. 63-101.

² Stutzer, O., and Noé, A. C., *Geology of Coal*, University of Chicago Press, Chicago, 1940, pp. 273-88.

³ Sprunk, G. C., and O'Donnell, H. J., *U. S. Bur. Mines, Tech. Paper 648* (1942), 67 pp.

⁴ Fuchs, W., *Die Chemie der Kohle*, Berlin, 1931, p. 416.

⁵ Thiessen, G., Ball, C. G., and Grotts, P. E., *Ind. Eng. Chem.*, **28**, 355-61 (1936).

quantities of minerals present in the original coal. One such table of possible forms of mineral matter postulated from ash constituents was presented by Marson and Cobb;⁶ it has often been quoted, and it is reproduced in Table I.

TABLE I

INORGANIC CONSTITUENTS OF COAL⁶

Inorganic Constituent	Forms in Coal
Silicon	Silicates, sand
Aluminum	Alumina in combination with silica
Iron	Pyrite and marcasite (sulfides) Ferrous oxide Ferrous carbonate Ferrous sulfate Ferric oxide Ferric sulfate Organic iron Iron silicates
	} in small quantities
Calcium	Lime, carbonates, sulfates, silicates
Magnesium	Carbonate, silicates
Sodium and potassium	Silicates, carbonates, chlorides (in small quantities)
Manganese	Carbonate, silicates
Sulfur (inorganic)	Pyrites and marcasite Ferrous sulfate Ferric sulfate Calcium sulfate
	} in small quantities
Phosphorus	Phosphates

Certain formulas, particularly the Parr unit coal formula and its modifications and simplifications, have been used to convert total ash values to total mineral-matter values for the purposes of correcting coal analyses, particularly calorific values, to the mineral-matter-free basis. In such correction formulas, use is usually made of the values for total sulfur, sometimes for pyritic sulfur, and occasionally of the values for carbonate and chlorides. The Parr unit of coal value⁷ uses the following relationship:

⁶ Marson, C. B., and Cobb, J. W., *Gas J.*, **171**, 39-46 (1925).

⁷ Parr, S. W., and Wheeler, W. F., *Univ. Illinois Eng. Expt. Sta. Bull.* **37**, 33 (1909).

$$MM = 1.08 \text{ ash} + 0.55 S$$

where *MM* represents mineral matter.

Ash analyses can be converted rationally to mineral-matter values only with an actual knowledge of the amount and quality of the minerals present in the coal. Gauger, Barrett, and Williams⁸ reported finding the minerals listed in Table II in seven samples of coal and three samples of washery refuse, all of unstated origin. No quantitative data were given as to the amount of minerals in the sample. On the basis of these mineralogical examinations, they calculated three ash analyses to the following minerals: pyrite, prochlorite, calcite, muscovite, kaolin, quartz, diaspore, and limonite, attributing most of the mineral matter to pyrite, muscovite, and kaolin. Five other ashes were recalculated to pyrite, gypsum, apatite, calcite, prochlorite, limonite, rutile, muscovite, kaolin, quartz, and diaspore.

Thiessen, Ball, and Grotts,⁹ on the basis of both the kind and proportion of mineral matter found in coal by petrographic examination, concluded that the separable mineral matter in both Pennsylvania coal and Illinois coal was composed of more than 99 percent of kaolinite, pyrite, detrital clay, and calcite. Ball⁹ found that more than 95 percent mineral matter in Illinois coal from West Frankfort, Franklin County, Illinois, consisted of the three minerals kaolinite, pyrite, and calcite. On this basis Thiessen¹⁰ calculated the 21 ash analyses presented in *U. S. Bureau of Mines Bulletin* 364¹¹ to pyrite, silica, calcite, kaolinite, and magnesium carbonate,

⁸ Gauger, A. W., Barrett, E. P., and Williams, F. J., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 226-35 (1934).

⁹ Ball, C. G., *Illinois State Geol. Survey, Rept. Investigations* **33** (1935), 106 pp.

¹⁰ Thiessen, G., *ibid.*, **32**, 27-39 (1934).

¹¹ Nicholls, P., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **364** (1932), 71 pp.

MINERAL MATTER IN COAL

TABLE II

RESULTS OF PETROGRAPHIC STUDY OF TEN SAMPLES OF COAL *

Name	Formula	Remarks
Pyrite	FeS_2	Found in all samples
Kaolin minerals	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$	Found in all samples
Chlorites:		
Prochlorite *	$2\text{FeO} \cdot 2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Found in all samples
Penninite *	$5\text{MgFe} \cdot \text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_3 \cdot 2\text{H}_2\text{O}$	Found in three samples
Muscovite	$\text{KNaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Found in all samples
Calcite	CaCO_3	Found in nine samples
Quartz	SiO_2	Found in all samples
Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Found in two samples
Limonite	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Found in seven samples
Magnetite	Fe_3O_4	Found in seven samples
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Found in all samples
Rutile	TiO_2	Found in two samples
Hematite	Fe_2O_3	Found in one sample
Tourmaline	Not constant; a complex aluminum borosilicate	
Siderite	FeCO_3	Found in two samples
Zircon	ZrSiO_4	Found in two samples
Garnet	$\text{Ca}_3\text{Al}_2\text{Si}_5\text{O}_{12}$	Found in one sample

* These two forms not positively identified, but two different chlorites were present and they were statively identified as penninite and prochlorite.

adding in the other items of the analysis, including the iron oxide in excess of that required to form pyrite with the determined quantity of pyritic sulfur.

Ball,⁹ as mentioned above, investigating the No. 6 Seam coal of Illinois, found that "More than 95 percent of the mineral matter is found to consist of but three minerals, calcite, pyrite, and kaolinite. The latter mineral occurs both in detrital clay and as a prominent filling in desiccation cracks and fusion cavities in the coal." Kaolinite, calcite, and pyrite were deposited after formation of the peat. The detrital mineral matter deposited during the peat formation consisted mainly of clay occurring as horizontal partings or bands in the coal or disseminated through its detrital layers. The other detrital minerals "consisted of the minerals commonly occurring in the sandstones, shales, and clays associated

with the coal." In the approximate order of their relative abundance in the coal column studied, these minerals were: quartz, feldspar, garnet, common hornblende, apatite, zircon, muscovite, epidote, biotite, augite, kyanite, rutile, staurolite, topaz, tourmaline, and chloritic material. Ball further stated, "The nonclay minerals, although always present, are quantitatively of little importance, invariably constituting less than 1 percent of the total separable mineral matter or less than 0.1 percent per 1 percent of the coal." The separable mineral matter made up 30 percent of the total mineral matter of the coal, but ash analyses indicated that the remaining 70 percent of mineral matter which was not separable by float-and-sink methods had the same composition and distribution as the separable minerals.

The clay constituent of coal has been

identified as kaolinite by Ball,¹² who has well described its properties and modes of occurrence.

In making the study of the mineral matter in the Illinois No. 6 Seam coal, Ball obtained a column of coal representing the entire thickness of the coal bed, divided it into small blocks, and examined and reported blocks individually.⁹ The separable mineral contents of the benches into which the coal is divided by the miner were found from the results of the examination of the individual blocks making them up and presented by Ball and Cady.¹³ These results are presented in Table III. It will be

thraxylon, bright coal, splint coal, and fusain are characterized by differences in both quantity and chemical and mineralogical compositions of the mineral matter they contain. Anthraxylons contain very little mineral matter, most of which is inherent; they generally contain from 1 to 3 percent ash. Those with the most ash owe their higher ash content to minute cracks filled with extraneous matter.

Sprunk and O'Donnell³ have presented the analyses of thirty-four anthraxylons from the United States, the ash contents of which ranged from 0.8 to 3.9 percent. They reported that anthraxylons with less

TABLE III

SEPARABLE MINERAL MATTER IN COAL FROM NO. 6 SEAM IN ILLINOIS¹²

Bench	Thick- ness inches	Number of Blocks *	Total Mineral Matter percent	Kaolinite		Pyrite		Calcite	
				In Coal percent	In Mineral Matter percent	In Coal percent	In Mineral Matter percent	In Coal percent	In Mineral Matter percent
V †	10.1	3	3.15	0.71	22.49	1.81	57.44	0.63	20.07
IV	30.7	20	1.49	1.33	89.53	0.09	6.01	0.07	4.46
III	44.5	45	2.51	2.02	80.56	0.32	12.72	0.17	6.72
BB ‡	1.6
II	12.3	10	7.30	2.97	40.73	0.10	1.35	4.23	57.91
I §	7.7	2	4.27	1.49	34.97	0.02	0.50	2.76	65.54
II-IV	89.1	75	2.79	1.90	68.27	0.21	7.44	0.68	24.29
I-V ¶	106.9	80	2.98	1.67	56.05	0.45	15.07	0.86	28.87

* Individual blocks from $\frac{1}{2}$ inch to 6 inches in thickness.

‡ Blue band, not included in sample.

|| Average representing thickness of mined coal.

† Top coal, not mined.

§ Bottom coal, not mined.

¶ Average representing total thickness of bed.

noted that there was great variation in the make-up of the mineral matter in the various benches.

MINERAL MATTER OF PETROGRAPHIC COMPONENTS

The petrographic components of coal, vitrain, clarain, durain, and fusain or an-

than 0.2 percent ash have been described. Lessing¹⁴ reported the ash content and the ash analyses of the four petrographic components of coal from the Thick Seam of South Staffordshire at the Hamstead Colliery as shown in Table IV. Lessing stated that "The high percentage of water-soluble and the low hydrochloric acid-insoluble in

¹² Ball, C. G., *Econ. Geol.*, **29**, 767-76 (1934).

¹³ Ball, C. G., and Cady, G. H., *ibid.*, **30**, 72-88 (1935).

¹⁴ Lessing, R., *J. Chem. Soc.*, **117**, 256-65 (1920); *Fuel*, **5**, 17-23, 69-76, 117-24 (1926).

TABLE IV

ASH ANALYSES OF PETROGRAPHIC COMPONENTS
OF THICK SEAM COAL ¹⁴

FUSAIN (Ash Content 15.59 percent)

	Soluble in Water percent	Soluble in Hydro- chloric Acid percent	Insoluble in Hydro- chloric Acid percent	Total percent
SiO ₂	0.00	0.78	8.06	8.84
Al ₂ O ₃	0.19	8.33	4.06	8.66
Fe ₂ O ₃				3.37
MnO				0.51
TiO ₂				0.04
CaO	10.03	46.64	0.33	57.00
MgO	0.41	0.89	0.00	1.30
Na ₂ O	0.65	2.59	3.24
K ₂ O	0.14	0.53	0.67
SO ₃	4.71	9.17	0.77	14.65
P ₂ O ₅
CO ₂	0.53	2.45 (diff.)	2.98
Total	16.65	71.88	13.22	101.26
Total by direct weighing	16.57	71.88	12.05	100.00

DURAIN (Ash Content 6.26 percent)

SiO ₂	Trace	1.46	49.08	50.54
Al ₂ O ₃	Trace	19.94	24.20	42.34
Fe ₂ O ₃				1.86
MnO				0.00
TiO ₂				0.44
CaO	1.47	1.85	0.37	3.69
MgO	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00
SO ₃	2.10	0.98	0.15	3.23
P ₂ O ₅
Total	3.57	24.28	73.50	101.60
Total by direct weighing	3.48	23.81	72.71	100.00

CLARAIN (Ash Content 1.22 percent)

SiO ₂	0.12	0.96	8.36	9.44
Al ₂ O ₃	0.10	12.66	7.86	16.58
Fe ₂ O ₃				3.31
MnO				0.23
TiO ₂				0.50
CaO	10.50	1.94	0.54	12.98
MgO	9.20	1.32	0.00	10.52
Na ₂ O	13.76	1.95	15.71
K ₂ O	0.00	0.00
SO ₃	31.73	0.45	32.18
P ₂ O ₅	0.00	0.01	0.00	0.01
Total	65.41	19.29	16.76	101.46
Total by direct weighing	65.24	17.86	16.90	100.00

TABLE IV—Continued

ASH ANALYSES OF PETROGRAPHIC COMPONENTS
OF THICK SEAM COAL ¹⁴

VITRAIN (Ash Content 1.11 percent)

	Soluble in Water percent	Soluble in Hydro- chloric Acid percent	Insoluble in Hydro- chloric Acid percent	Total percent
SiO ₂	Trace	0.76	5.32	6.08
Al ₂ O ₃	3.11	13.44	2.40	15.49
Fe ₂ O ₃				3.09
MnO				0.13
TiO ₂				0.24
CaO	12.42	2.46	0.34	15.22
MgO	1.04	0.83	0.00	1.87
Na ₂ O	16.12	1.55	17.67
K ₂ O	0.20	0.00	0.20
SO ₃	28.62	1.49	0.78	30.89
P ₂ O ₅	Trace
CO ₂	6.69	6.69
Total	68.20	20.53	8.84	97.57
Total by direct weighing	69.52	20.46	10.02	100.00

the ashes from clarain and vitrain prove that they present the original plant ash."

In the same coal, the ash contents of the petrographic ingredients usually tend to increase in the order: vitrain, clarain, durain, and fusain. The high ash content of the fusain shows up particularly in the high ash content of the fine dust produced in the mining and preparation of coal, for example, the dust recovered from dedusting plants.¹⁵

Though in general alumina, silica, iron oxide, lime, and magnesia comprise over 95 percent of coal ash, certain coals contain appreciable and much higher than usual contents of such other components as manganese, zinc, lead, cadmium, copper, and gold. Jensch¹⁶ reported the percentages of metallic oxides in six coal ashes from Upper Silesia shown in Table V.

¹⁵ Thiessen, G., *Trans. Am. Inst. Mining Met. Engrs.*, **119**, 277-86 (1926).

¹⁶ Jensch, E., *Chem.-Ztg.*, **10**, 1271-370 (1887).

TABLE V

COMPOSITIONS OF COAL ASHES FROM UPPER SILESIA COALS¹⁶ IN PERCENTAGE OF THE TOTAL ASH

	Coal Numbers					
	1	2	3	4	5	
Manganese oxide	1.33	0.42	2.84	1.17	1.43	0.20
Zinc oxide	0.26	0.37	1.12	0.09	0.55	0.86
Lead oxide	0.021	0.069	0.058	0.037	0.082	0.056
Cadmium oxide	0.008	0.001	0.003	0.005	0.004	0.002

1. Unwashed lump coal from Schmieder mine, Porembe.

2. Coal from Schmieder mine washed in Friedenshütte coal washery.

3. Dust coal from Schmieder mine.

4. Dust coal from Wolfgang mine (Valentin shaft near Ruda).

5. Dust coal from the Gotthard shaft of the Paulus mine near Morgenroth.

6. Coal screenings from the Aschenborn shaft of the Gottessegen mine near Antonienhütte.

Stone¹⁷ reported coals near Cambria, Wyoming, which contain gold attaining a value of \$2.00 a ton. Thirty-one shipments of coke showed an average gold content of \$2.46 and silver content of \$0.28 per ton at \$20 per ounce for gold and \$0.65 per ounce for silver. The gold in the Cambria coal was believed to have come from an overlying sandstone, the gold content of which is about 0.1 ounce per ton and is present largely in the shaley coal high in ash.

Zilbermintz¹⁸ determined the vanadium content of more than 500 samples of coal, with the results shown in Table VI. In a number of coals of Jurassic Age, vanadium pentoxide contents of ashes of as much as 8 percent were found. A study of the occurrence of vanadium in these coals indicated that it was due to infiltration, the high contents coming from a decay of the basic rocks of the Ural Range in which numerous segregations of rocks rich in

¹⁷ Stone, R. W., *U. S. Geol. Survey, Bull.* 499, 63-4 (1912).

¹⁸ Zilbermintz, V. A., *Compt. rend. acad. sci. U.R.S.S.*, N.S. 3, 117-20 (1935).

TABLE VI

OCCURRENCE OF VANADIUM PENTOXIDE IN THE ASH OF RUSSIAN COALS¹⁸

Locality of Occurrence	Number of Determinations	Average Content of Vanadium Pentoxide	Range of Vanadium Pentoxide Content
		percent	percent
Donets Basin	266	0.08	0.02 to 0.34
Tkivibuli	39	0.13	0.07 to 0.27
Tkvarcheli	17	0.13	0.05 to 0.15
Khumara	15	0.10	0.04 to 0.16
Pechora Basin	50	0.08	0.02 to 0.31
Karaganda	8	0.06	0.04 to 0.08
Suchan	6	0.07	0.04 to 0.11
Sakhalin	4	0.10	0.08 to 0.11
Cheremkhovo	5	0.06	0.03 to 0.09
Kuznetzk Basin	4	0.09	0.08 to 0.11
Moscow Basin	3	0.12	0.09 to 0.16
Spitzbergen		0.09	0.07 to 0.11

vanadium occur. The same author and his associates have also studied the distribution of beryllium, germanium, and nickel in various Russian coals.¹⁹

Coals contain many other elements, some in extremely minor traces.²⁰ It has been reported that barium occurs very commonly in the coals of Britain, ranging from 0.1 to 6 percent of the ash.²¹ In certain "special" British coals, Jones and Miller found the titania content to range from 4.76 to 24.3 percent, and the nickel oxide content from 0.1 to 10.3 percent.²² Both germanium and gallium have been reported

¹⁹ Zilbermintz, V. A., and Rusanov, A. K., *ibid.*, 2, 27-31 (1936). Zilbermintz, V. A., Rusanov, A. K., and Kostrikin, V. M., *Akad. V. I. Vernadskomu k Pyatiletseyu Nauch. Deyatelnosti*, 1, 169-90 (1936). Zilbermintz, V. A., *Mineral. Suir'e*, 11, No. 6, 16-26 (1936). Nazarenko, V. A., *Trav. lab. biogéochim. acad. sci. U.R.S.S.*, 4, 265-70 (1937). Vorob'ev, A. L., *Compt. rend. acad. sci. U.R.S.S.*, 28, 250-1 (1940).

²⁰ Goldschmidt, V. M., and Peters, C., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1933, 371-86. Thilo, E., *Z. anorg. Chem.*, 218, 201-9 (1934). Burkser, E. S., Kondoguri, V. V., Kaputsin, N. P., and Potapov, P. P., *Ukrain. Khim. Zhur.*, 9, 441-5 (1934).

²¹ Reynolds, F. M., *J. Soc. Chem. Ind.*, 58, 64-8 (1939).

²² Jones, J. H., and Miller, J. M., *Chemistry & Industry*, 1939, 237-45.

present in British and Australian coals.²³

Goldschmidt²⁴ has said:

It is remarkable that the rare elements which are found concentrated in the ashes of coals may have very different chemical properties, for instance, we find beryllium, strontium, barium, boron, scandium, yttrium, lanthanum, and the lanthanides (elements of atomic numbers 51-71); zirconium, vanadium, cobalt, nickel, molybdenum, uranium, copper, zinc, gallium, germanium, arsenic, antimony, cadmium, tin, iodine, lead, bismuth; silver, gold, rhodium, palladium, platinum (not yet tested or incomplete data, among others, thorium, indium, thallium, selenium, tellurium). In many cases all these elements, or most of them, have been concentrated in the same ashes.

²³ Morgan, G. T., and Davies, G. R., *ibid.*, **1937**, 717-21. Cooke, W. T., *Trans. Roy. Soc. S. Australia*, **62**, 318-9 (1938).

²⁴ Goldschmidt, V. M., *Ind. Eng. Chem.*, **27**, 1100-2 (1935).

Table VII, presented by Goldschmidt, gives data for a number of elements commonly concentrated in coal ashes in order to illustrate their degree of enrichment, as compared with their average percentage, as far as is known by reliable data, in the common rocks of the earth's crust. The data refer to percentages and are representative only for such ashes as show the phenomenon of enrichment. Three main stages of the enrichment process were postulated: (1) concentration during the life of the plants, (2) concentration during decay of the plants, and (3) concentration during mineralization of the coal. Examples of these three stages of enrichment as demonstrated by analytical data were presented. Fuchs²⁵ also presented similar

²⁵ Fuchs, W., *Ind. Eng. Chem.*, **27**, 1099-1100 (1935).

TABLE VII

RARE ELEMENTS IN ASHES OF COAL AND IN THE EARTH'S CRUST²⁴

Element	Maximum Percentage	Average		Factor of Enrichment	
		Percentage of "Rich" Ashes	Percentage in Earth's Crust	Maximum	Average of "Rich" Ashes
Be	0.1	0.03	0.0002 to 0.001	100 to 500	30 to 150
B	0.3	0.06	0.0003	1,000	200
Sc	0.04	0.006	0.0003 to 0.0006	70 to 130	10 to 20
Co	0.15	0.03	0.004	40	8
Ni	0.8	0.07	0.01	80	7
Zn	1	0.02	50	...
Ga	0.04	0.01	0.001 to 0.0015	30 to 40	7 to 10
Ge	1.1	0.05	0.0004 to 0.0007	1,600 to 2,800	70 to 120
As	0.8	0.05	0.0005	1,600	100
Y	0.08	0.01	0.001*	80	10
Zr	0.5	0.02	25	..
Mo	0.05	0.02	0.0015	30	13
Sb	0.1	0.02
Sn	0.05	0.02	0.005	10	4
Pb	0.1	0.0016	70	..
Bi	0.003
Ag	0.005 to 0.001	0.0002	0.00001	50 to 100	20
Au	0.00002 to 0.00005	0.0000005	40 to 100	..
Rh	0.000002
Pd	0.00002
Pt	0.00007

data for brown coals as shown in Tables VIII and IX.

TABLE VIII

ELEMENTS FOUND IN GERMAN BROWN-COAL ASHES ²⁵

Gravimetric Analysis		Spectrophotographic Analysis	
	percent		10 ⁵ × percent
Ca	35.56	Cu	100 to 1,000
Fe	10.74	Ba	10 to 100
Mg	4.86	Pb	10 to 100
Si	3.31	Sr	10 to 100
Al	1.60	Bi	10 to 100
Na	2.30	Ni	10 to 100
K	0.19	Zn	10 to 100
Mn	0.35	Ti	10 to 100
P	Traces	Au	1 to 10
C, O, H, N, S	Also present	Ga	Traces
		Ge	Traces

TABLE IX

AMOUNTS OF EIGHTEEN ELEMENTS IN COAL ASH, THE EARTH'S CRUST, AND VARIOUS FORMS OF ORGANIC LIFE ²⁵

	Coal Ash percent	Earth's Crust percent	Organisms percent
Ca	35.6	3.4	1 to 10
Fe	10.7	4.7	10 ⁻¹ to 10 ⁻²
Mg	4.8	2.0	10 ⁻² to 10 ⁻¹
Mn	0.35	0.1	10 ⁻³ to 10 ⁻²
	3.31	25.7	10 ⁻¹ to 1
Al	1.6	7.5	10 ⁻² to 10 ⁻¹
Na	2.3	2.6	10 ⁻² to 10 ⁻¹
K	0.2	2.4	10 ⁻¹ to 1
P	Trace	0.1	10 ⁻¹ to 1
Cu	10 ⁻⁴ to 10 ⁻³	10 ⁻² to 10 ⁻¹	10 ⁻³ to 10 ⁻¹
Ba	10 ⁻⁵ to 10 ⁻⁴	10 ⁻² to 10 ⁻¹	?
Pb	10 ⁻⁴ to 10 ⁻³	10 ⁻³ to 10 ⁻²	10 ⁻⁴ to 10 ⁻³
Sr	10 ⁻⁵ to 10 ⁻⁴	10 ⁻² to 10 ⁻¹	
Bi	10 ⁻⁵ to 10 ⁻⁴	10 ⁻⁴ to 10 ⁻³	
Ni	10 ⁻⁵ to 10 ⁻⁴	10 ⁻² to 10 ⁻¹	
Zn	10 ⁻⁵ to 10 ⁻⁴	10 ⁻³ to 10 ⁻²	10 ⁻² to 10 ⁻¹
Ti	10 ⁻⁵ to 10 ⁻⁴	0.5	10 ⁻⁴ to 10 ⁻³
Au	10 ⁻⁶ to 10 ⁻⁵	10 ⁻⁶ to 10 ⁻⁵	10 ⁻⁶ to 10 ⁻⁵

THE ORIGIN OF COAL MINERAL MATTER

Coal mineral matter had its origin in the inorganic constituents of the vegetation from which it was formed and in mineral matter brought in from outside the deposit where it was formed. As has been men-

tioned, the first is termed inherent and the second adventitious mineral matter.

The inherent mineral matter is much smaller in quantity than and different in composition from the mere inorganic residue of the coal-forming plants. This fact is due to reuse of the inorganic elements by succeeding vegetation and to leaching of inorganic constituents by the waters percolating and flowing through the peat bog during deposition and through the deposit during coalification. The percolating waters may be presumed to have an increased dissolving action on the inorganic constituents because of their content of humic acids, carbon dioxide, and other products of decay.

Owing to the differences in solubilities and reactions of the inorganic elements present in the plants, these elements do not contribute to the coal mineral matter in proportion to their presence in the plants. The mineral matter in anthraxylon or vitrain is largely inherent and low in quantity.

The adventitious mineral matter brought in during the formation of the peat deposit was largely detrital clay together with the minor quantities of the minerals making up the rocks surrounding the basin in which the peat bog was forming.

Lessing¹⁴ compared the alumina-silica ratios of the ashes from fusain, durain, clarain, and vitrain with the alumina-silica ratios of the ashes from various lycopods to determine whether the inference that the high alumina content of durain might be due to its derivation from lycopods was plausible. He concluded that the inference was disproved and that "durain ash is identical with clay, whilst clarain and vitrain closely resemble plant ashes."

The variations in ash contents with increasing depths in peat bogs presented in the literature show no consistency, prob-

ably because of the radical differences in the nature of the bogs.

A moss, reed, sedge peat from Velen was reported by Fischer, Schrader, and Friedrich,²⁶ to contain 1.8, 1.7, and 1.8 percent ash at depths of 0.0, 0.9, and 1.8 meters, respectively, while a woody peat from Lauchhammer was reported by the same authors to have ash contents of 7.1, 6.8, and 6.6 percent at increasing depths.

Waksman²⁷ analyzed a peat deposit 6 meters in thickness and found its ash content almost constant at 1 percent, except for the topmost and bottom portions which contained 2.0 and 2.8 percent ash, respectively.

All that these and other such data show is that the ash contents of peats and brown coals vary widely in amount just as do those of bituminous coals. The ash contents of peats also are dependent upon the type of bog, whether low moor or high moor; reed, moss, or wooded. From the standpoint of investigating the origins of normal banded bituminous coals, interest is centered in the wooded low moor type, not particularly common in Europe. Most of the peat bogs in Europe being of the high moor moss type, the experimental work on peat by European investigators has, therefore, been largely on peat of this type. In any event, it is generally conceded that the coal ash due to the mineral matter (inorganic elements) in the coal-forming plants is but a few percent of the coal. In vitrains (anthraxylon) and other low-ash coals or coal components, it may be a major part of the ash content; for high-ash coals it is a minor proportion.

The major components of the adventitious mineral matter in coal are detrital clay, kaolinite, pyrite, and calcite. Of these the detrital clay was brought into

the bog as such; the others were for the most part formed in the deposit, either in the peat stage or later from their components.

The detrital clay was washed in from the surrounding higher ground by water and probably to a minor extent brought in by air. The amount washed in at any time depended upon the differences in elevation, intensity and amount of precipitation, water-level conditions and drainage in the bog, and the nature of the surrounding land. Detrital clay is important only in the clay partings of a coal seam. Ball²⁸ found the detrital clay in Illinois No. 6 Seam coal to be largely kaolinite with a smaller amount of a sericite-like mineral. Concerning the relative abundance of secondary kaolinite and detrital clay, Ball and Cady²⁸ have said:

Visual examination and microscopic counts of the clay constituents, however, indicate that the detrital clay is important only in the clay partings, and that it does not compose more than 25 percent of the total clay and kaolinite portion of the mineral matter. Clay partings are largely fortuitous in character and in general separate certain benches of the coal seam.

Sprunk and O'Donnell concluded:

Uniform partings were formed by extensive flooding of level swamp surfaces. The mineral matter was deposited quickly without interrupting the growth of the swamp plants. Irregular partings were deposited if the swamp surface was uneven or if the peat bog was subjected to differential subsidence.⁸

The underclays may possibly furnish some evidence about the nature and origin of the detrital clay in the coal. Grim and Allen²⁹ found the underclays under Illinois coals to consist largely of kaolinite and illite. After reviewing previously advanced theories of their origin, Grim and Allen concluded that mineralogical and textural

²⁶ Fischer, F., Schrader, H., and Friedrich, A., *Ges. Abhandl. Kenntnis Kohle*, 5, 530-40 (1920).

²⁷ Waksman, S. A., *Am. J. Sci.*, 19, 32-54 (1930).

²⁸ See p. 22 of ref. 9.

²⁹ Grim, R. E., and Allen, V. T., *Bull. Geol. Soc. Am.*, 49, 1485-514 (1938).

data favored an aqueous environment of deposition. They conceived the possibility that the underclays were deposited as a montmorillonitic mud; those deposited in a marine environment rich in alkalis, particularly potash, absorbed potash and after burial changed to illite, whereas those deposited in brackish or nonmarine, relatively alkali-free, environment were prevented from changing to illite and, therefore, changed to kaolinite. A mixture of illite and kaolinite would develop from material containing limited amounts of potash. They argued against post-accumulation infiltration of alkalis. They further concluded that the underclays did not appear to have been altered, after accumulation and before burial, by processes similar to those forming modern soils. This they stated also argues against leaching of alkalis from illitic deposits to yield kaolinites. That the underclays were not subject to weathering or soil-forming agencies would permit correlation of their nature with the detrital clay in the coal itself. Sprunk and O'Donnell³ stated that "The kinds of minerals in partings of clays and shales are similar to those observed by Grim³⁰ in the Pennsylvania underclays."

Kaolinite and calcite in desiccation cracks, cleats, joints, and the cavities in bands and lenses of fusain are of secondary origin deposited from circulating waters,¹² largely after the peat stage of formation.

The origin of the pyrite and marcasite in coal is more complex and varied; it is discussed in detail in Chapter 12. Briefly, the finely disseminated pyrite is probably due to the activities of sulfur-depositing bacteria. The larger and massive deposits are due to the precipitation of ferrous sulfide by interaction of hydrogen sulfide from the decay of plant material and iron compounds in solution in the bog water

with later conversion of the ferrous sulfide to pyrites. Possibly some pyrite was formed by reduction of ferrous sulfate by organic matter.

Many coals contain highly mineralized nodular concretions, usually near the roof of the seam, consisting of petrified or fusainized plant remains. The mineral matter is pyrite or calcite and occasionally siderite.³ The origin and nature of the concretions have been well described by Stutzer and Noé.² Coal balls were mineralized during the peat stage—just how is still open to speculation.

The minor detrital minerals in coal were transported into the peat bed from outside. They are disseminated, not localized, in small detrital grains. The minor secondary minerals were deposited from water which had picked up these minerals or their components from other beds. Because of its highly absorptive nature, colloidal coal would tend to absorb such mineral matter. In addition, the possible formation of metal humates must not be overlooked.

Coal close to the surface may, in addition, carry a wash of clay, hydrated iron oxide, or carbonates, or ferrous sulfate brought in by percolating surface waters and deposited in cracks, joints, and cleats. Often these compounds affect the appearance of the coal out of all proportion to the amount of mineral matter they add.

Boulders, though occurring comparatively rarely, are of considerable interest because of the speculations to which they give rise concerning peat bog conditions. Their occurrence has been discussed and the theories concerning the agencies by which they were brought into the bog have been reviewed by Stutzer and Noé² and by Raistrick and Marshall.¹ These authors also have discussed the unusual geological conditions causing clay veins, horsebacks, holidays, sandstone channels, and the like.

³⁰ Grim, R. E., *Bull. Am. Cer. Soc.*, **14**, 113-9, 129-34, 170-6 (1935).

CHAPTER 15

THE FUSION, FLOW, AND CLINKERING OF COAL ASH A SURVEY OF THE CHEMICAL BACKGROUND

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This survey is concerned with those physicochemical properties of coal ashes which are involved in clinkering and the related phenomena associated with the fusion and flow of the ash-forming mineral matter. The subject is considered under three main headings: (1) the fusibility of coal ash; (2) the viscosity and surface tension of coal-ash slags; and (3) the relationship of fusibility, viscosity and surface tension to various types of operating trouble.

The thesis of the survey, in so far as it has a thesis, is twofold: first, that the behavior of the ash in clinkering and related phenomena is, primarily, a function of its chemical rather than its mineralogical composition, and second, that, in the modern boiler furnace, the properties of the molten slag, and particularly its behavior on cooling, rather than the original fusion temperature of the ash-forming minerals, determine the nature of the operating difficulties encountered.

THE FUSIBILITY OF COAL ASH

That clinkers are composed of a mixture of fused or partly fused ash or ash-forming mineral matter has been recognized for as long as there has been a clinkering problem. Consequently it is not surprising

that, in striving to develop a laboratory procedure which would permit some estimate of the extent of clinker formation to be anticipated when burning a given coal in a given piece of equipment under a given set of operating conditions, the early investigators should have attempted to measure a property of the ash comparable to the melting point of pure compounds. It was, of course, recognized that the ash was a complex mixture which could not have a definite melting point and that, therefore, some arbitrary degree of melting or of mobility of the slag formed from the ash would have to be adopted in lieu of a melting point if the fusibility of the ash were to be expressed by a single temperature. The recognition of this limitation and the prior development of the familiar Seger cones commonly used in the ceramic industry account for the fact that all the early workers utilized a test piece molded from the finely ground ash and similar in shape to the Seger cones.

It is worthy of note that the method which has become the standard in the United States still utilizes a test piece in the form of a triangular pyramid, one face of which is normal to the base, although in other respects the procedure displays a much greater degree of refinement than the

initial attempts to make measurements which would be reproducible in the same or different laboratories and permit of interpretation in terms of actual service conditions. Although the method has been subjected to no little criticism, as will appear later, it has found wide applicability and more general usefulness than most empirical tests and, in addition, it has been shown to give results in good agreement with two other empirical tests which, in the mechanics of their application, appear to be rather different from it.

The three methods of test in common use are the A.S.T.M. standard method,¹ the method developed by Sinnatt, Owles, and Simpkin,^{2, 3} and the method of Bunte and Baum^{4, 5, 6, 7, 8} which has been applied extensively not only in Germany but also in Japan. In the succeeding sections of this part of the survey these three methods will be considered in detail, and some attention will also be given to less familiar procedures.

METHODS OF MEASUREMENT

The A.S.T.M. Standard Method. This method was developed by members of the

¹ Standard Method D271-37, *Am. Soc. Testing Materials Standards*, 1939, Pt. III, p. 15.

² Sinnatt, F. S., Owles, A. B., and Simpkin, S. N., *J. Soc. Chem. Ind.*, **42**, 266-72T (1923); *Colliery Guardian*, **125**, 1131 (1923). Simpkin, S. N., and Sinnatt, F. S., *J. Soc. Chem. Ind.*, **44**, 197-200T (1925). The method of Sinnatt, Owles, and Simpkin is not the method of the British Standards Institution (B. S. I. No. 453), which is a cone fusion method substantially identical with the A.S.T.M. Standard method.

³ Sinnatt, F. S., *New Intern. Assoc. Testing Materials*, September, 1931.

⁴ Bunte, K., and Baum, K., *Gas- u. Wasser-fach*, **71**, 97-100, 125-30 (1928).

⁵ Bunte, K., and Reerink, W., *ibid.*, **72**, 832-9 (1929).

⁶ Bunte, K., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 231-40 (1928).

⁷ Bunte, K., *New Intern. Assoc. Testing Materials*, September, 1931.

⁸ Reerink, W., and Baum, K., *Wärme*, **53**, 746-51, 766-71 (1930).

staff of the United States Bureau of Mines. It is based on very elaborate and painstakingly acquired experimental evidence, which is described, together with applications to the ash of a very large number of coals, in numerous publications.^{9, 10, 11} The history of the development of the method is given in *Bulletin* 129 of the United States Bureau of Mines,⁹ which includes a detailed summary of the work of earlier investigators. Appended to the bulletin is a bibliography of 187 titles covering not only fusibility and clinkering of coal ash but also the physical chemistry of slags and silicates, melting and softening temperatures of oxides, sulfides, and slags, pyrometric cones, pyrometers and the measurement of high temperature, and laboratory furnaces for high-temperature work.

Prior to the studies described in *Bulletin* 129 it was not at all uncommon for softening temperatures determined on the same ash by different laboratories to differ by several hundred degrees. Because most coal ashes contain appreciable amounts of iron which, at the temperatures involved, can exist in three states of valence (metallic, ferrous, or ferric iron), depending on

⁹ Fieldner, A. C., Hall, A. E., and Feild, A. L., *U. S. Bur. Mines, Bull.* **129** (1918), 146 pp.

¹⁰ Nicholls, P., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **364** (1932), 72 pp.

¹¹ Fieldner, A. C., and Hall, A. E., *J. Ind. Eng. Chem.*, **7**, 399-406, 474-S1 (1915). Fieldner, A. C., and Feild, A. L., *ibid.*, **7**, 742-7, S29-S3 (1915). Fieldner, A. C., and Selvig, W. A., *Fuel*, **5**, 24-33 (1926). Selvig, W. A., *Coal Age*, **15**, 12 (1919). Selvig, W. A., Nicholls, P., Gardner, W. A., and Muntz, W. E., *Mining and Met. Investigations, U. S. Bur. Mines, Carnegie Inst. Tech., & Mining & Met. Advisory Boards, Coop. Bull.*, **29** (1926), 63 pp. Selvig, W. A., Brown, O. C., and Fieldner, A. C., *Coal Age*, **17**, 177-80, 225-30 (1920). Selvig, W. A., and Fieldner, A. C., *Chem. & Met. Eng.*, **20**, 629 (1919); *U. S. Bur. Mines, Bull.* **209** (1922), 119 pp.; *Coal Age*, **15**, 1086 (1919). Selvig, W. A., Ratcliff, W. C., and Fieldner, A. C., *ibid.*, **15**, 698 (1919); *Chem. & Met. Eng.*, **20**, 274-6 (1919).

the oxidation potential of the environment, the workers at the Bureau of Mines believed that the large variations noted above were to be ascribed, primarily, to the oxidation potential of the furnace atmosphere. They chose to work with test pieces molded from the finely ground ash into the form of Seger cones. Duplicate cones were heated in several different types of furnaces such that the furnace atmospheres varied from strongly oxidizing to strongly reducing. The results obtained showed clearly that the temperature required to produce a given degree of deformation of the test piece was, in general, much higher when the atmosphere was either 100 percent oxidizing or 100 percent reducing than when the ratio of oxidizing to reducing gases present was in the vicinity of unity.

It was also noted that the tall, slender Seger cone shape did not provide a satisfactory test piece because the viscosity and surface tension of the liquids produced in the fusion process often tended to draw the cone into a globule. Consequently many cones, instead of bending over smoothly until their apices touched the cone pat, fused into lumps of irregular shape; if the softening temperature was defined as that at which the tip of the cone touched the pat, such cones had no definite softening temperature. Consequently the proportions of the cones were changed by decreasing the height and broadening the base. Three temperatures were then defined in terms of three states of deformation: (1) the initial deformation temperature, i.e., the temperature at which the tip of the cone became definitely rounded under the constraint of the surface tension of the liquid phase; (2) the softening temperature, i.e., the temperature at which the cone had fused into an approximately spherical lump; (3) the fluid temperature, i.e., the temperature at which the cone

lost all definite form and flowed out over the pat.

The effect of variations in furnace atmosphere having been demonstrated qualitatively, a quantitative investigation was made. For this purpose a molybdenum furnace was constructed in which the oxidation potential of the atmosphere could be adjusted by controlled gas flow. In one series of experiments mixtures of hydrogen and water vapor were used, and in another mixtures of carbon monoxide and carbon dioxide. Both series of experiments served to show that ashes containing considerable amounts of iron reached the standard states of deformation described above at higher temperatures when the environment consisted of either 100 percent oxidizing gas or 100 percent reducing gas than when it consisted of mixtures of intermediate oxidizing potential. In general small quantities of oxidizing gas introduced into an environment of reducing gas or small quantities of reducing gas introduced into an environment of oxidizing gas produced a marked lowering of the initial deformation, softening, and fluid temperatures but over the range from about 30 percent oxidizing gas to about 70 percent oxidizing gas the effect of changes in oxidizing potential of the environment was not significant. From fundamental physicochemical considerations this range in gaseous composition was shown to correspond to an oxidation potential such that ferrous oxide was the stable phase for the iron, and analytical determinations of the forms of iron in cones fused in environments falling within this composition range indicated that substantially all the iron was actually in the ferrous condition. On the other hand, analyses of cones fused in completely reducing environments showed substantially all the iron in the metallic state, and cones fused in completely

oxidizing environments contained principally ferric iron.

The existence of this wide range over which the composition of the gaseous environment may vary without substantially altering the temperatures at which the cones reach the standard states of deformation is, obviously, a decided advantage. Moreover, since measurements within this range give minimal values the results obtained will not be misleading in the direction of causing overestimation of the refractoriness of ashes so tested. Most important of all is the fact that this range in gaseous composition probably corresponds fairly closely to that which exists in the hottest parts of a fuel bed and, consequently, determinations made in such an environment should be a better indication of the fusion characteristics which the ash would exhibit under service conditions than determinations made in any other gaseous environment.

In view of the relatively wide range over which the composition of the gaseous environment might be permitted to vary, it appeared to the Bureau of Mines investigators that, if a gas-fired furnace were used with a deficient air supply, the results should agree closely with those obtained in the more expensive molybdenum furnace with a 50-50 oxidizing-reducing gas atmosphere. Kaplan¹² had modified the "No. 3 melter's furnace" for use in ash-fusibility measurements, and E. B. Ricketts, Research Engineer, New York Edison Company, had used this furnace for a number of years. The furnace had also been used at the Pittsburgh Experiment Station of the United States Bureau of Mines. Therefore comparisons were made between results obtained with it, when operated with just enough air to maintain the de-

sired rate of heating, and results obtained on the same ashes when using the molybdenum furnace with a controlled atmosphere. A satisfactory agreement was found between the two sets of determinations, and the gas furnace was adopted as the standard apparatus.

In addition to the foregoing major considerations the size and proportions of the test pieces, the fineness of grinding of the ash, the method of ashing, and the manner of molding and mounting the cones were investigated. The effect of the rate of heating was also carefully studied.

The results of these investigations were utilized to formulate the A.S.T.M. standard method.¹ Subsequently two additional gas furnaces have been approved by the A.S.T.M. for ash-fusion determinations: the Denver Fireclay furnace, which differs in no essential respect from the No. 3 melter's furnace, both being large, pot-type furnaces, and the Barrett fusion furnace,¹³ which is a small furnace of the horizontal muffle type. Only six cones can be tested simultaneously in the Barrett furnace as against ten in the larger pot furnaces; however, owing to its smaller heat capacity, it cools more rapidly, and consequently more runs can be made with it in a given time. The furnace is so constructed that the cones are viewed against a background which is always somewhat cooler than the cones, so that observation of the degree of deformation is facilitated. Committee D-5 of the American Society for Testing Materials supervised tests of this furnace and has approved its use in ash-fusion measurements.¹⁴ It is believed to be inadvisable to test more than five cones at one time, but some laboratories take ad-

¹² Kaplan, B. B., *Ind. Eng. Chem.*, **16**, 847-8 (1924).

¹³ Barrett, E. P., *Proc. Am. Soc. Testing Materials*, **35**, Pt. II, 627-36 (1935).

¹⁴ *Ibid.*, **37**, Pt. I, 404 (1937).

vantage of the size of the large pot furnaces to crowd in as many as ten cones.

Fish, Taylor, and Porter¹⁵ endeavored, with only fair results, to adapt the Remmey oxyacetylene furnace to the measurement of coal-ash-softening temperatures. They placed the ash cone on a pat with a number of standard pyrometric cones and took as the softening temperature the pyrometric cone equivalent of the standard cone, the tip of which had just touched the pat when the ash cone became spherical. No advantage appears to be derived from the use of standard pyrometric cones, especially as an optical pyrometer controls the rate of heating. More recently Gilmore and Young¹⁶ compared results obtained in the Remmey furnace with those obtained in the No. 3 melter's furnace and concluded that, when the furnace is properly installed and operated, it meets the requirements of the A.S.T.M. standard method.

The conclusions reached and the mode of procedure described in *Bureau of Mines Bulletin* 129 have stood the test of time remarkably well. Those who developed the procedure recognized that it was not altogether satisfactory as an index of clinker trouble. In fact, the bulletin specifically stated that a procedure which permitted measurement of the viscosity of the coal-ash slag over a wide temperature range by some appropriate method, such as that applied by Feild¹⁷ to blast-furnace slags, would probably permit a closer correlation between test results and clinker trouble in fuel beds. However, the method has been found to be of very considerable practical value, and a minimum ash-softening tem-

perature is specified in nearly all large purchases of coal.

As will appear later, all investigators of coal-ash fusibility, regardless of the particular method of test, have confirmed the observations made on the effect of the composition of the gaseous environment. However, not all those who have worked with test pieces of pyramidal shape have accepted all the details of the A.S.T.M. standard method. Kreulen,¹⁸ for example, did not recommend the use of the dextrin binder and, in spite of the objections noted in *Bulletin* 129, continued to use a tall, slender cone. He confirmed the effect of the gaseous environment reported by the American workers and noted that the addition to the cone of coke from the coal which was the source of the ash being tested raised the softening temperature. Care should be taken to insure complete ashing not only to avoid reduction of iron to the metallic state, with a consequent elevation of the softening temperature, but also because the presence of even small amounts of combustible residue may result in swelling and intumescence of the cones.

Pacukov,¹⁹ discussing the A.S.T.M. standard method, suggested that the tests might better be made on the slag resulting from fusion rather than on the ash. This suggestion, together with others of a similar nature, will be considered later in this survey.

Pieters²⁰ and Pieters and Smeets²¹ utilized a test piece, similar to a Seger cone with a truncated apex, formed by suspending the pulverized ash in water and casting

¹⁵ Fish, F. H., Taylor, F. M., and Porter, J. L., *Ind. Eng. Chem., Anal. Ed.*, **4**, 442-5 (1932).

¹⁶ Gilmore, R. E., and Young, R. J., *Bur. Mines, Mines and Geology Branch, Dept. Mines and Resources, Ottawa, Canada, Memorandum Series*, **71** (May, 1939).

¹⁷ Feild, A. L., *U. S. Bur. Mines, Tech. Paper* **157** (1916), 29 pp.

¹⁸ Kreulen, D. J. W., *Chem. Weekblad*, **24**, 599-602 (1927), **25**, 192-4 (1928), **33**, 291-2 (1936).

¹⁹ Pacukov, N. G., *Izvest. Teplotekh. Inst.*, No. **10**, 34-6 (1927), No. **5**, 18-28 (1928).

²⁰ Pieters, H. A. J., *Chem. Weekblad*, **27**, 331-4 (1930), **33**, 510-20 (1936).

²¹ Pieters, H. A. J., and Smeets, G., (a) *Het Gas*, **52**, 171-2 (1932); (b) *ibid.*, **53**, 446-8 (1933).

in a mold. The end point was taken as the temperature at which the top of the bending cone touched the pat. The procedure appears to possess no advantage over the A.S.T.M. standard method and is open to the same objection as all other methods employing cones that are tall relative to their base area.

The Method of Sinnatt, Owles, and Simpkin. The method developed by Sinnatt, Owles, and Simpkin,^{2,3} utilized a cylinder of ash $\frac{1}{32}$ inch in diameter formed by extrusion through a die, the rod so obtained being cut into pieces $\frac{3}{16}$ inch in length. These pieces were mounted vertically and heated in a quartz tube which formed the horizontal core of a magnesia-lined gas furnace. Because the quartz core was impervious to combustion gases it was necessary to control the atmosphere in the tube. This was done by means of a mixture of hydrogen and steam. The temperature at which the test piece fused to an approximately spherical lump was called the melting point.

Dawe²² devised a means for controlling the composition of the hydrogen-steam mixture, and Dawe and Falkner²³ described an electric furnace, equipped with a saturator to produce a proper atmosphere, which was adapted to making this test.

It appears that the difference in shape of the test piece or in the mode of its production affects the results obtained. Nicholls and Selvig¹⁰ tabulated the results of measurements made in a gas furnace conforming to the A.S.T.M. standard. Their data showed that of 42 ashes tested both in the cone form and in the form of extruded rods only 4 gave identical results. Eleven sam-

ples gave higher results in the extruded rod form than in the cone form and 27 gave lower results. The average difference for those giving positive deviations was plus 55° F; for those giving negative deviations, minus 90° F. The algebraic average deviation of the rod forms from the cone forms was minus 44° F. The maximum positive deviation was plus 120° F, and the maximum negative deviation minus 120° F.

The data indicated that cylindrical test pieces formed by extrusion in general deform to a substantially spherical form at a lower temperature than hand-molded cones. This may be ascribed, primarily, to the method of forming rather than to the difference in shape. The cylindrical test pieces being formed by extrusion are probably subjected to higher pressures, with a resultant closer packing of the individual particles, than the hand-molded cones. The softening temperature does not represent an equilibrium condition but, on the contrary, markedly depends on the rate of solution of solid particles in a liquid phase; consequently, any treatment which tends to accelerate the rate of solution will tend to lower the temperature at which an approximately spherical state of deformation is reached. Close packing of the particles is such a treatment, and it appears, therefore, that softening-temperature measurements made on extruded rods might be expected to give somewhat lower results than those made on hand-molded cones.

On the whole, the discrepancies noted in the results obtained by the alternative methods of preparing the test pieces do not appear to be of marked practical significance, for, as will be shown later, the correlation between the results of ash-fusion measurements and the clinker trouble experienced in actual practice is not close enough to permit a reliable prediction as

²² Dawe, A., *Fuel*, **12**, 271-5 (1933).

²³ Dawe, A., and Falkner, C. W., *ibid.*, **13**, 230-6 (1934).

to which of two ashes differing by only 100° F in softening temperature will give the greater amount of clinker trouble in a fuel bed under service conditions.

The method of Sinnatt, Owles, and Simpkin has been studied by Tweedy²⁴ and by Wallsom,²⁵ but neither they nor any of the others who have utilized this method have brought to light any important factors involved in obtaining consistent results which were not considered by those who developed the A.S.T.M. standard method.

The Method of Bunte and Baum. The method of Bunte and Baum^{4, 6, 7} and its modification by Bunte and Reerink^{5, 8} are somewhat more elaborate than either of the methods previously described. A cylindrical test piece 25 millimeters in diameter and 30 millimeters high is mounted vertically in a carbon resistance furnace between two pieces of electrode carbon. The upper piece is movable, and its position is recorded on a rotating drum so that a record of height versus time, which can be converted to a record of height versus temperature, is obtained.

If the initial deformation temperatures and the softening temperatures are located on the melting curves determined in this way it is found that they bear no characteristic relationship to changes in slope of the curves. Bunte^{6, 7} believed that the melting curves obtained can be grouped into three classes and can be interpreted as indicating the occurrence of chemical reactions some of which may increase the refractoriness of the ash. Curves which show no halting points and in which the collapse of the test piece occurs smoothly over a rather narrow temperature range are taken

as indicating that the ash is homogeneous and that no chemical reactions occur.

It should be remarked that the carbon resistance furnace provides an atmosphere comparable to that of a gas furnace because determinations made on cones in both such furnaces agree well. Bunte and Baum⁵ gave comparative data on this point.

The method has been used by a number of observers, occasionally with some modifications. Abramov²⁶ applied it to Russian coal ashes and discussed the mechanism of fusion. Baum²⁷ discussed earlier methods in the light of the information obtained from melting curves. Bro²⁸ used the method and discussed the melting processes at length but without bringing out any new considerations. Kosaka and his coworkers²⁹ applied the method of Bunte and Baum extensively in the study of the fusion characteristics of Japanese coal ashes but without in any way affecting the conclusions derived from earlier work. Pieters and Smeets^{21a} compared results obtained by this method with cone-deformation measurements. The A.S.T.M. standard method, the British method, and the method of Bunte and Baum were summarized and discussed by Sinnatt³ in a paper which gives data to show that results obtained by all three methods are in substantial agreement.

²⁶ Abramov, S. N., *Zavodskaya Lab.*, **6**, 81-3 (1937); *Coke and Chem. (U.S.S.R.)*, **7**, 15-8 (1937); *Chimie & industrie*, **38**, 874 (1937).

²⁷ Baum, K., *Glückauf*, **64**, 1733-41 (1928).

²⁸ Bro, Louis, *J. usines gaz*, **56**, 422-31 (1932); *Chaleur et ind.*, **15**, 37-57 (1934), **19**, 583-9 (1938).

²⁹ Kosaka, Y., *J. Fuel Soc. Japan*, **14**, 119-24 (1935). Kosaka, Y., and Toda, H., *J. Soc. Chem. Ind., Japan*, **37**, 98-101B, 188-9B (1934); *J. Soc. Chem. Ind., Japan*, **40**, Suppl. binding, 179-80, 180-2 (1937). Kosaka, Y., Toda, H., and Kitagawa, C., *J. Soc. Chem. Ind., Japan*, **37**, 606-10B, 610-4B (1934); *J. Soc. Chem. Ind., Japan*, **39**, Suppl. binding, 36-8, 38-40 (1936).

²⁴ Tweedy, S., *Gas World*, **103**, Coking Sect., 99-104 (1935).

²⁵ Wallsom, H. E., *Fuel Economist*, **7**, 313-6 (1932).

Methods Not Generally Accepted as Standard. The micropyrometer method is an adaptation of a method described by Burgess³⁰ for determining the melting points of minute quantities of material. The apparatus was described in detail and the results obtained with it were compared with those given by the A.S.T.M. standard method by Fieldner, Selvig, and Parker.³¹

In this method an amount of finely ground ash equal in volume to about the head of a pin is placed on a platinum strip which serves as the heating element. The strip is surrounded by a small metal furnace which permits the maintenance of a controlled atmosphere. The furnace is provided with a thin glass window through which the ash is observed by means of a microscope which is also equipped to function as an optical pyrometer. The temperature at which the ash fuses around its edges, as indicated by a thin white border spreading around the specimen, is observed and recorded as the initial fusion temperature. The final fusion temperature is taken as that at which fusion is complete as indicated by the disappearance of the last dark spot when the specimen is viewed through the microscope. The platinum strip is heated electrically, the rate of temperature rise being controlled by a rheostat.

All investigators who have worked with the micropyrometer have been in substantial agreement that the results obtained with it cannot be used interchangeably with those obtained by the A.S.T.M. standard method. Bunte and Baum,⁵ who compared the micropyrometer method with the American, British, and German methods, found substantial agreement among the three standard methods but no correlation with the

results obtained with the micropyrometer. De Graaf³² incorporated certain mechanical features intended to increase accuracy and simplify operation, but Selvig³³ has demonstrated, with the cooperation of five other laboratories, that the method is unsatisfactory.³⁴ Hudson³⁵ compared 27 samples using the de Graaf apparatus and the standard gas furnace; he concluded that the de Graaf apparatus gave a fair correlation in the range from 2,300 to 2,500° F. Jones, Farmer, Brewer, and Porter³⁶ stated that the micropyrometer did not give uniform results unless the ash was applied to the strip in the form of a pellet of uniform size and shape. If this was done the results were somewhat lower for high-fusing ashes and higher for low-fusing ashes than those obtained by the gas-furnace method. However, they stated that the results obtained conformed more closely to those observed in practice and recommended the micropyrometer for routine testing of the quality of coal deliveries. Vassar³⁷ considered the micropyrometer satisfactory, stating that it gave reproducible results that could be correlated with observations under actual fuel-bed conditions. This, he said, is more important than a correlation with the A.S.T.M. standard method.

In a sense, the apparatus developed by Bramslev³⁸ was a micro modification of

³² Eimer and Amend, New York, N. Y. *Bull.* **402** (1929).

³³ Selvig, W. A., *U. S. Bur. Mines, Repts. Investigations*, **3003** (1930), 17 pp.

³⁴ See also Brennan, J. J., Mitchell, D. F., Tierney, F. P., and Thompson, W. C., *Ind. Eng. Chem., Anal. Ed.*, **9**, 106-11 (1937).

³⁵ Hudson, Ray P., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 324-5 (1934).

³⁶ Jones, M. C. K., Farmer, H., Brewer, J. E., and Porter, H. C., *Ind. Eng. Chem., Anal. Ed.*, **2**, 325-8 (1930).

³⁷ Vassar, H. S., *Proc. Am. Gas Assoc.*, **1929**, 1099-102.

³⁸ Bramslev, E. R., *Gas- u. Wasserfach*, **79**, 943-6 (1936).

³⁰ Burgess, G. K., *U. S. Bur. Standards, Sci. Paper* **198** (1913).

³¹ Fieldner, A. C., Selvig, W. A., and Parker, W. L., *J. Ind. Eng. Chem.*, **14**, 695-8 (1922).

the method of Bunte and Baum, differing from it in that the deformation of the test piece was followed photographically so that no external mechanical force entered into the deformation of the test piece, which was so small that only a few centigrams of ash was required as a sample. The deformation of the molded specimen was recorded by projecting upon a fiber in a camera the image, magnified 13.5 times, of a slit which covered the test specimen. The slit image was reflected into the camera from the mirror of a galvanometer actuated by a thermocouple in the ash-fusion furnace so that the image of the slit at all times occupied a position that was a function of the furnace temperature. A screen in the camera provided reference lines on the film in order that changes in length of the specimen could be read directly from the photographic record. The data so obtained are comparable to the melting curves of Bunte and Baum, and their interpretation will be considered along with those of Bunte and Baum in connection with the significance of viscosity and surface tension of coal-ash slags.

Diepschlag³⁹ described a method for measuring the "temperature of dripping" of slags, etc. The procedure has not been applied by other observers to the study of coal ash, and it seems unlikely that it would show any very useful correlation with practical experience in furnaces.

Dolch⁴⁰ and Dolch and Pöschmüller⁴¹ devised a micro method in which a small amount of the ash was placed on the flattened junction of a platinum-platinum rhodium thermocouple. In the original Dolch and Pöschmüller method heat was supplied from below by an arc lamp and in Dolch's

modification by an arch of resistance wire. The specimen was observed from above with a microscope. Agreement within 20 Centigrade degrees in the vicinity of 1,600° C with accepted melting points of known substances was claimed by the authors.

Ludmila⁴² used the method and claimed agreement with known melting points within 10 Centigrade degrees at 1,000° C. However, Šimek, Coufalík, and Beránek⁴³ claimed that the method gave low results because of thermal losses through the thermocouple. The procedure has not been generally adopted. It appears to be less satisfactory than the micropyrometer.

Mertens⁴⁴ used a graphite tube furnace, the tube being surrounded with finely powdered wood charcoal. The tube served as the heating element of a carbon resistance furnace. An atmosphere of nitrogen was provided to minimize oxidation of the tube. Test pieces in the form of small tetrahedra were placed on small iron trays within a magnesia tube closed at one end, and the tube was then put in the hot zone of the furnace. Temperatures were read with an optical pyrometer. So far as the writer is aware, no other investigators have used Mertens' method.

Summary. Three methods for measuring the fusion or softening temperature of coal ash which yield results in substantial agreement are the A.S.T.M. standard method, the method of Sinnatt, Owles, and Simpkin, and the German Gas Institute method. In all three an attempt to estimate relative viscosities of the melting

³⁹ Diepschlag, E., *Feuerungstechn.*, **21**, 115-7 (1933).

⁴⁰ Dolch, M., *Wärme*, **54**, 255-7 (1931).

⁴¹ Dolch, M., and Pöschmüller, E., *Feuerungstechn.*, **18**, 149-51 (1930).

⁴² Ludmila, J., *Mitt. Kohlenforsch. Inst. Prag*, **1**, 82-8 (1931-3).

⁴³ Šimek, B. G., Coufalík, F., and Beránek, Z., *Feuerungstechn.*, **22**, 1-6 (1934); *Mitt. Kohlenforsch. Inst. Prag*, **2**, 34-51 (1935).

⁴⁴ Mertens, E., *Bull. fédération ind. chim. Belg.*, **3**, 292-301 (1924).

ashes is made by noting the temperature interval between two or more standard states of deformation, but the introduction by Bunte and Baum of means for recording the degree of deformation automatically provides more complete information on this point than the three basic methods.

With the exception of these three methods and of the micropyrometer method, none of the procedures that have been proposed have been adequately checked against actual fuel-bed performance under controlled conditions and none of them, the micropyrometer method included, shows a definite correlation with the three basic methods.

ASH FUSIBILITY AS A FUNCTION OF COMPOSITION

*Theoretical Considerations.*⁴⁵ Bunte⁶ discussed his method of obtaining melting curves, described in the preceding section of this survey, in part, as follows:

It seems to me that from these curves, it follows that it is impossible—and why it is impossible—to draw a conclusion as to the fusion point from the relation of the basic and acid constituents. The old maxim *corpora non agunt nisi fluida* is also valid here. Calcium oxide, for instance (from CaCO_3), aluminum oxide (Al_2O_3), and silica are practically unmeltable in the furnace. Their mechanical mixtures behave in the same way until a faster-melting constituent dissolves them. The calcium aluminum silicates (e.g., clay, garnet), on the contrary, which can have the same analytical composition melt easily.

Although Bunte's argument is very persuasive, nevertheless the fact remains that

a number of rather successful correlations between chemical composition of coal ash and its softening temperature have been found. The reason may be, in part, that the correlations that have been published have been confined largely to coals from a fairly restricted area, principally the states of Pennsylvania, Ohio, Illinois, West Virginia, and Kentucky, as a consequence of which it would not be surprising to find that the ash-forming minerals present were fairly similar, that is, that the ash-forming minerals contained in most of the coals differed in relative amount but that the number of mineral species involved was rather small.

It is not proposed to consider here the nature of the ash-forming minerals contained in coals from these regions because the subject is fully discussed in Chapter 14. Suffice it to say that the silica and alumina which concern Bunte are not present as such in large amounts in most coals from the above regions. The large proportions of these oxides which are determined in the ordinary chemical analysis of ash are contributed, not by the simple oxides, but by kaolin minerals such as kaolinite or by complex aluminosilicates, such as the chlorites or muscovite mica, which contain alumina and silica combined in the kaolin ratio. It is true that quartz (SiO_2) and diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) do occur in small amounts as shown by direct observation and as indicated by the fact that many coal ashes do not contain silica and alumina in the kaolin ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.17$). However, it can be shown that the softening temperature of a coal ash depends primarily on its chemical composition (provided that the ash is prepared for testing in a standardized manner), and that, within fairly narrow limits, a coal ash can be regarded, so far as its softening temperature is concerned, as though it were

⁴⁵ In this section reference will not, in general, be made to original work on phase equilibria. The reader is referred to "A Compilation of Phase Rule Diagrams of Interest to the Ceramist and Clay Technologist" by F. P. Hall and Herbert Insley (*J. Am. Ceram. Soc.*, **16**, 455-568 [1933]), which contains all the equilibrium diagrams referred to in this survey together with original references.

kaolin contaminated by a mixture of metallic oxides.

Consider a simple two-component system, such as that shown in Fig. 1, in which there are no intermediate compounds and no solid solutions. The curve AEB is the liquidus of the system, and TET is the eutectic isotherm. If mechanical mixtures of

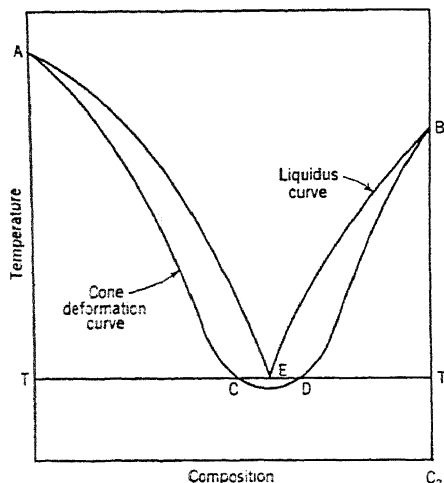


FIG. 1. Comparison of liquidus and cone deformation curves for a generalized two-component system.

the components C_1 and C_2 are molded into cones, and cone-deformation temperatures determined according to some accepted technique, a cone deformation temperature-composition curve will be obtained which has a minimum at the eutectic composition. The actual deformation temperatures obtained will depend primarily upon the rate of heating if other factors are kept constant.

If, in addition to mixing the components, we allow reaction and solution to occur by heating the mixtures to some definite temperature, for some definite length of time before the cone deformation is measured, a different curve will be obtained. Conse-

quently, if we are to speak of the relationship between cone-deformation and equilibrium diagrams, it is necessary to suppose that the cones are always prepared from materials which have been subjected to some standard treatment before deformation temperatures are determined. In the discussion which follows it will be assumed that the mixtures of C_1 and C_2 have been heated to a temperature somewhat below the eutectic for several hours before final grinding and molding into cones, a procedure not dissimilar to that involved in ashing a coal preparatory to measuring softening temperatures.

Assuming that the cones have been prepared from powders that have received the standard treatment specified above, it is possible to determine qualitatively what the nature of the deformation temperature-composition curve must be. If the components C_1 and C_2 are pure, the points A and B will constitute the two ends of the curve; the point E will likewise lie on the curve.

It is apparent that for the cones to reach the standard state of deformation it is unnecessary for them to consist entirely of liquid. The exact amount of liquid to produce the standard deformation depends primarily on the viscosity and surface tension of the liquid. However, it is certain that the cone-deformation temperature for any composition will lie below the liquidus.⁴⁶ On either side of the eutectic composition is a range of compositions all of which show substantially the same deformation temperature. The limits of this range are the compositions at which the cone contains just enough liquid to produce the standard state of deformation at the eutectic temperature. These limits are

⁴⁶ It is true that some of the feldspars do not flow until heated well above their melting points, but the generalization, nevertheless, is true for coal ashes and fireclays.

ASH FUSIBILITY AS A FUNCTION OF COMPOSITION

shown in Fig. 1 as points *C* and *D*. In practice, where materials from natural sources are of interest, this portion of the cone-deformation curve will not follow the straight line *CED* but, owing to the presence of small amounts of impurities, will follow the arc *CD*.

Figure 2 shows an application of this theory to two coal ashes, the analyses of which are shown in Table I. If the rela-

TABLE I

COMPOSITION OF COAL ASHES

Sample No.	1	2
	percent	percent
SiO ₂	49.1	36.3
Al ₂ O ₃	42.0	31.4
Fe ₂ O ₃	2.8	27.5
CaO	2.3	2.1
MgO	0.4	0.3

tive amounts of silica, alumina, and alkaline-earth oxides are expressed on the basis

$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{MgO} = 100$ percent

the data of Table II are obtained. Legitimate objections may be raised to classifying magnesium as an alkaline earth, but for

TABLE II

COMPOSITION OF COAL ASHES ON THE IRON OXIDE-FREE BASIS

Sample No.	1	2
	percent	percent
SiO ₂	52.4	51.9
Al ₂ O ₃	44.7	44.7
CaO + MgO	2.9	3.4

the purposes of this discussion it is convenient to do so. It is also instructive to calculate the ratio of silica to alumina for these ashes and to compare it with that of kaolin. Such calculation yields:

Sample No.	1	2	Kaolin
SiO ₂ /Al ₂ O ₃	1.17	1.16	1.17

These calculations are of interest because they show that these two ashes, which appear to be quite different according to the ash analysis, were very closely related. Both contained silica and alumina in the kaolin ratio, and both contained about 3 percent of alkaline-earth oxides, so that the

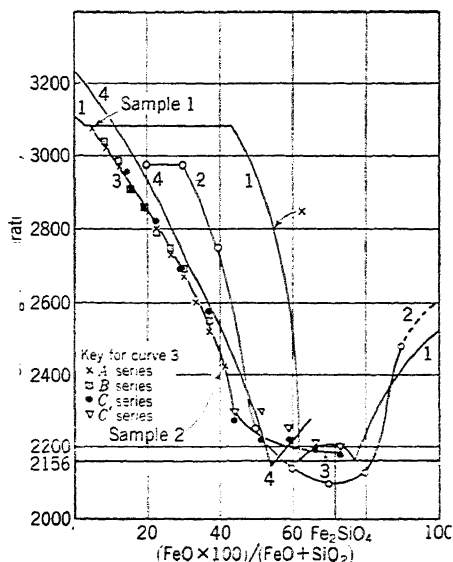


FIG. 2. Relationship of softening temperature to composition for a particular ferrous oxide coal-ash system.

difference between them consisted simply in a relatively larger amount of ferric oxide in sample 2 than in sample 1. Moreover, a petrographic examination of sink fractions, at high specific gravities, of the coals from which these ashes were derived showed the presence of very little quartz or diaspore.⁴⁷ Consequently we are justified in assuming that the alumina and silica in these ashes were present chiefly as kaolin.

The considerations brought out in the

⁴⁷ Gauger, A. W., Barrett, E. P., and Williams, F. J., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 226-36 (1934).

theoretical discussion show that if the powders from which ash cones are to be made are finely ground and intimately mixed, and are brought to the same standard state before the cones are made, then: (1) the softening temperatures can depend only upon the composition and not upon the manner in which the composition is obtained; and (2) the softening temperature must be closely related to the phase-equilibrium diagram for a system of the components which make up the ashes.

The major components are silica, alumina, and ferrous oxide.⁴³ We may neglect, for the moment, the alkaline earths and a small amount of alkalis (not shown in the analysis). The ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ has not been studied, nor has the binary system $\text{Al}_2\text{O}_3\text{-FeO}$. However, so long as relatively large amounts of silica are present we can assume that the binary system $\text{SiO}_2\text{-FeO}$ will control the behavior of the cones except that the immiscible liquid region of the equilibrium diagram will not appear on the cone-deformation diagram and that, consequently, lowering of the softening temperature will occur in a regular manner as the ferrous oxide content increases.

The results of experiments designed to test the correctness of these assumptions are shown in Fig. 2. Curve 1 is the liquidus of the system $\text{SiO}_2\text{-FeO}$. Curve 2 was obtained by adding ferric oxide to ash 1 in such amounts that, after reduction to ferrous oxide in the ash-fusion furnace, the relative amounts of silica and ferrous oxide would be those shown in the figure. The ferric oxide was merely mixed with ash 1 by grinding in a mechanical mortar for 15 minutes.

⁴³ Shown in the ash analysis as ferric oxide, but it will be remembered that the conditions of the A.S.T.M. standard method effect substantially complete reduction of ferric iron to ferrous.

Although curve 2 closely approximates the liquidus it appears anomalous because it reflects the two-liquid region on the diagram and the fluxing action of ferrous oxide is much less than would be expected for percentages of ferrous oxide up to 50 percent of the ferrous oxide plus silica present. The theoretical considerations presented earlier in this discussion show that this result was to be anticipated because the ferric oxide was merely mixed mechanically with the ash. To obtain a result characteristic of coal ashes it is necessary to bring the powders to the standard state of intimate mixture and partial reaction toward equilibrium which characterizes coal ash prepared for test according to the A.S.T.M. standard method.

Because sample 1 and sample 2 were practically identical in composition, except for their difference in iron content, it was possible to compare the effect of increasing the iron oxide content in two different ways: (1) by mixing samples 1 and 2 in various proportions; and (2) by the direct addition of iron oxide to ash 1.

The *A* series of Fig. 2, curve 3, was prepared by mixing ashes 1 and 2 in nine different proportions. The *B* series was prepared by mixing the coals from which these ashes came in such proportions that the resulting ashes would have the same compositions as the corresponding points of the *A* series. To be sure of obtaining intimate mixing of the ferric oxide which was added to ash 1 to make the *C* series, the following procedure was adopted: the required weight of ash was suspended in distilled water, and a dilute solution of ferric nitrate was run into it from a buret until the required amount of iron was present; the iron was then precipitated with ammonium hydroxide buffered with ammonium chloride, after which ammonium oxalate was added to prevent the loss of lime and mag-

nesia by solution; the precipitates were filtered and the filter papers transferred to crucibles for ignition.

All the samples of the A, B, and C series were ignited at 850°C in an electric muffle and then ground in a mechanical mortar before being molded into cones; that is, they were all "ashed" according to A.S.T.M. specifications. Care was taken to keep the temperature and time of ashing constant for all samples. The C' series was obtained by the addition of Fe₂O₃ to ash 2, by the same technique as was followed for the A series.

The data presented in Fig. 2 and Table III clearly show that, when all the samples

TABLE III

DEVIATION OF MEASURED SOFTENING TEMPERATURES FROM CURVE 3

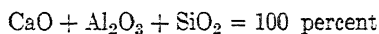
Cone	A Series °F	B Series °F	C Series °F	C' Series °F
Sample 1	0			
Mixture 1	0	15	25	
Mixture 2	0	15	15	
Mixture 3	-15	-15	0	
Mixture 4	-5	-5	35	
Mixture 5	-15	-25	-40	-10
Mixture 6	-20	0	-5	65
Mixture 7	-20	0	20	40
Mixture 8	-20	-20	0	10
Mixture 9	-20	10	-10	0
Sample 2	0			

were brought to the same standard initial condition, the softening temperatures were a function of the composition and were independent of the way in which it was attained. Moreover, these data constitute strong evidence that the procedure by which the results were related to the equilibrium diagram is generally applicable to clays and other inorganic mixtures which are of the same mineralogical nature, that is, which may be regarded as impure kao-

lin. The procedure would not be quantitatively applicable to diasporic clays or to mixtures of oxides unless these mixtures could be brought to the same standard state as the ashes and synthetic mixtures used here.

The evidence for the applicability of this procedure to clays as well as coal ashes is provided by curve 4 of Fig. 2. This curve summarizes the data of Rieke⁴⁹ on cone deformation temperatures for the system kaolin-FeO. Rieke's results averaged about 60 degrees higher than curve 3 of Fig. 2. This difference is readily accounted for by the 3 percent of lime and the 1.5 percent of alkalis which ash 1 contained. It will be observed that the minimum in Rieke's curve occurs at too small a percentage of ferrous oxide. In view of the evidence thus far presented, this point may be in error.

The system CaO-Al₂O₃-SiO₂ is of interest both to the coal chemist and to the clay technologist. Figure 3 shows the portion of the equilibrium diagram of special interest to workers in these two fields. If the compositions of fireclays and coal ashes are expressed on the basis



the other components being neglected, it is found that the fireclays fall in the field of mullite, except for a small percentage of samples, high in alumina, which fall in the field of corundum. The same is true of the ashes from Pennsylvania and West Virginia coals, but, owing to the frequent occurrence of relatively large percentages of lime, some of the ashes fall in the field of anorthite. In the figure the compositions marked by circles are those which were chosen for a study of cone deformation-composition relations in a ternary system. Ashes having these compositions were

⁴⁹ Rieke, R., *Sprechsaal*, **16**, 229-32 (1910); *J. Am. Ceram. Soc.*, **16**, 555 (1933).

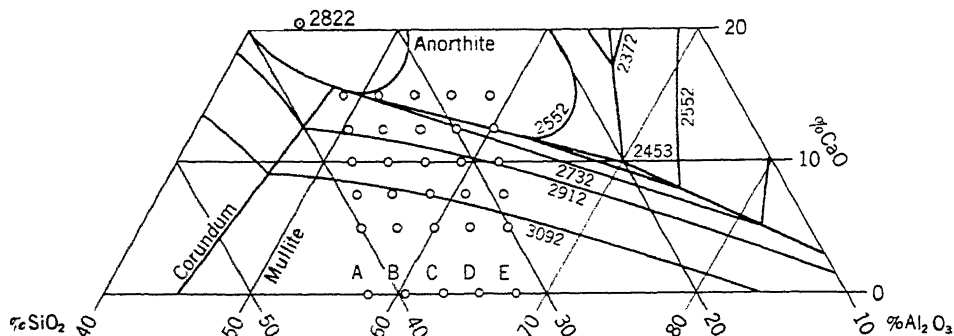


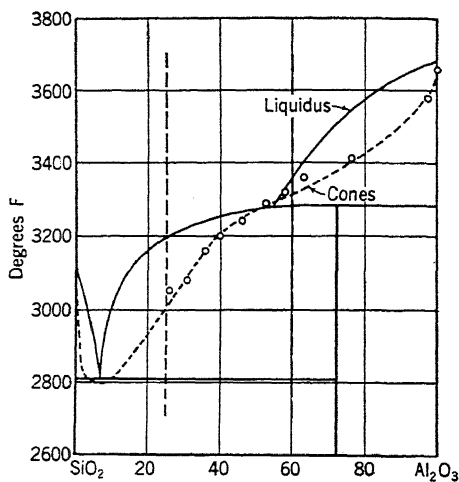
FIG. 3. A portion of the system lime-alumina-silica.

made by the addition of lime and silica to ash 1. The silica was added as anhydrous silicic acid; the lime, by suspending the solid mixture in distilled water and adding the appropriate amount of a dilute solution of calcium nitrate from a buret. The calcium was precipitated as oxalate, and the mixtures were filtered, ignited, and ground as in the experiments with the binary system.

In order to compare the results with the equilibrium diagram the effect of the small amount of iron present in ash 1 was corrected for by assuming that its effect was linear and equivalent to 30° per percent, an assumption justified by the data of Fig. 2. In view of the inaccuracy involved in ash-softening measurements it suffices to assume that the percentage of ferric oxide in all samples was 2 percent, and all the measured softening temperatures were therefore increased by 60° for purposes of comparison with the equilibrium diagram.

Because of the lime content of ash 1, it was not possible to make lime-free mixtures. The points on the alumina-silica boundary were obtained from the data of Fairchild and Peters⁵⁰ (Fig. 4). Figure 5 compares the liquidus temperatures with the cone-deformation temperatures for the

five different alumina-silica ratios, labeled A, B, C, D and E, respectively, in Fig. 3. Figure 6, A and B, compares liquidus and cone-deformation temperatures for the five different alumina-silica ratios with lime

FIG. 4. The system alumina-silica.⁵⁰

kept constant at 12.5 and 15 percent, respectively. All the softening temperature-composition curves are exactly of the form which would be anticipated from the theoretical considerations previously presented.

From the data it may be concluded that:

1. The fusion characteristics of coal ashes and of fireclays are related to their

⁵⁰ Fairchild, C. O., and Peters, M. F., *J. Am. Ceram. Soc.*, 9, 723-4 (1926).

compositions in the same manner, and, as long as their mineralogical compositions are such that they can be regarded as impure kaolins, their cone-deformation temperatures will vary with their compositions in the manner indicated by the data.

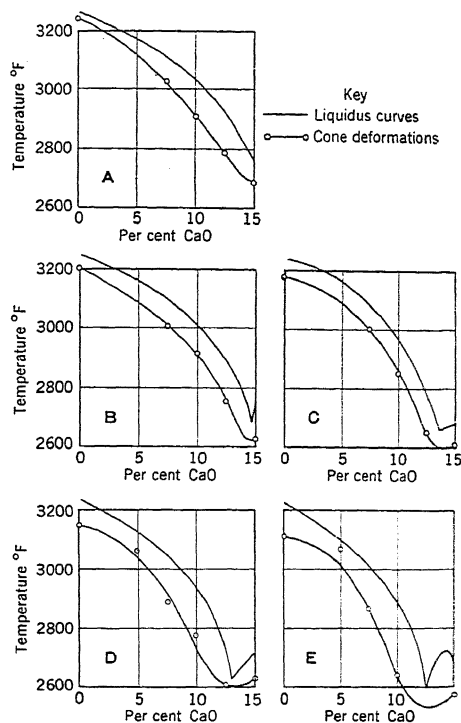


FIG. 5. Effect of lime on the softening temperatures of silica-kaolin mixtures.

2. The cone-deformation temperatures of mineral mixtures, however complex, are closely related to the liquidus temperatures of a system of the same components provided that the mixtures are always brought to the same standard state before measurements are made.

3. The differences between curves 2 and 3 of Fig. 2 suggest that reaction occurs in the solid state at a temperature of 850°C . Consequently, if concordant results are to

be obtained between different laboratories, it is important that coal samples be ashed at a standard temperature for a standard length of time.

General or Qualitative Relationships.

The preceding outline of the factors involved in coal-ash fusion makes it possible to examine critically some of the more re-

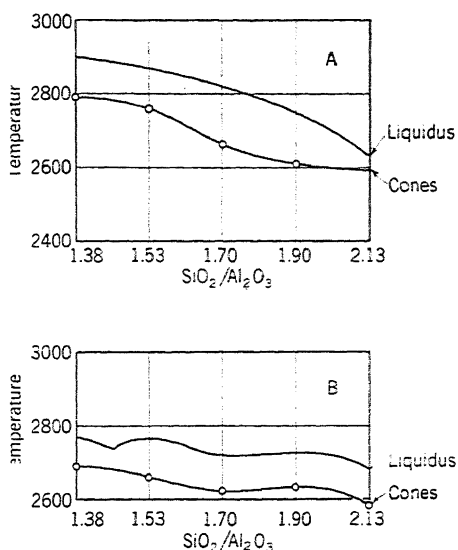


FIG. 6. Effect of silica-alumina ratio on softening temperatures of lime-kaolin mixtures.

cent publications which discuss the effect of one or more components on ash-softening temperature without attempting to set up a coherent system of correlation with analytical data. Papers describing more or less quantitative correlations will be discussed later.

Kosaka and his coworkers²⁹ investigated the influence of chemical composition on the fusibility of the ash of 56 Japanese coals. They reported that the composition of refractory ashes, i.e., those with softening temperatures in excess of $1,400^{\circ}\text{C}$ ($2,552^{\circ}\text{F}$) fell within the following limits:

silica greater than 50 percent, alumina greater than 25 percent, ferric oxide less than 10 percent, and lime less than 10 percent. They reported that plotting the percentage of any single component against the softening temperature indicated no definite relationship. They also stated that ashes containing 10 and 20 percent of lime and ferric oxide respectively and having a silica to alumina ratio greater than 2, or ashes containing over 30 percent lime plus ferric oxide and having a lime to ferric oxide ratio greater than unity, fuse below 1,250° C (2,282° F). Also, if lime or ferric oxide exceeded 20 percent its fluxing effect was decreased, and this phenomenon was more pronounced in respect to iron than in respect to lime. Moreover, they stated that these relations were less pronounced in a reducing atmosphere than in an oxidizing one.

The writer has never attempted to compare the effects of composition on softening temperatures as measured in oxidizing and in reducing atmospheres, but it appears that a less definite correlation under oxidizing conditions can only signify that the oxidizing potential of the environment varied considerably in Kosaka's measurements and, since the measured softening temperatures fell rapidly with the introduction of small amounts of reducing gases into an oxidizing atmosphere, it is probable that the results obtained in what Kosaka called an oxidizing atmosphere were a function not only of the composition of the ashes but also of the composition of the gaseous environment.

After an extended study of the effects of lime and ferric oxide on the fusion of coal ash in an oxidizing environment Kosaka and his coworkers reported that:

1. Ferric oxide mechanically mixed with coal ash decreased the softening temperature of three samples, the effect being

small after the ferric oxide content reached 20 percent.

2. On three other samples ferric oxide had little effect or increased the softening temperature.

3. The first three samples had relatively high softening temperatures; the latter three, lower softening temperatures.

4. For all six ashes additions of lime lowered the softening temperatures up to 25 to 35 percent lime, after which the softening temperature increased.

5. Additions of both lime and ferric oxide indicated that ashes containing considerable amounts of ferric oxide require a large amount of lime to produce a lowering of the softening temperature, but in the presence of considerable amounts of lime a small addition of ferric oxide was effective.

6. The ratio of silica to alumina seemed to be very important in determining the fluxing effect of lime and ferric oxide.

In considering these results, it is important to realize that they were determined in an oxidizing environment and that Kosaka was interested in the practical problem of removing ash from a slag-tap furnace. In short, his approach to the problem was empirical rather than theoretical, and, of course, the previous discussion of the effects of iron on ashes of varying lime-alumina-silica proportions does not apply in the absence of a reducing atmosphere comparable to that maintained in the A.S. T.M. standard method for determining softening temperature.

The system $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ has been studied by Hansen, Brownmiller, and Bogue;⁵¹ the melting relationships are very complex, involving, as they do, solid solution and incongruent melting. The quaternary system which would include

⁵¹ Hansen, W. C., Brownmiller, L. T., and Bogue, R. H., *J. Am. Chem. Soc.*, **50**, 396-406 (1928).

silica has not been studied even empirically so that it is impossible to present even a semitheoretical background for Kosaka's observations. In summing up his observations it should be remarked that, however useful they may have been for his own purposes, they are of little value in relating composition of ashes to their A.S.T.M. softening temperatures.

Lefebvre and Boulant⁵² studied about 30 samples of coals from northern France. They made the interesting observation that ashes obtained by prolonged incineration in a muffle contained neither ferric oxide nor ferrosferric oxide but calcium ferrite. They also stated that additions of ferric oxide, silica, or lime lowered the softening temperature and that additions of alumina and kaolin increased it. These observations are to be anticipated in view of the discussion already presented. They reported that additions of magnesia produced effects dependent upon the composition of the ash. If much iron was present there was formed magnesium ferrite, which rendered the ash more refractory. The formation of magnesium ferrite in a complex system such as a coal ash under the conditions of measurement used in determining ash-softening temperatures may be questioned. In general, it appears that magnesia behaves substantially like lime in its effect on the softening temperature, which is not surprising in view of the similarity of the equilibrium diagrams of the systems $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ in the composition ranges covered by the ashes of most coals.

Actually the fluxing action of magnesia on the kaolin minerals should be very similar to that of lime, but cones in the magnesia-kaolin system appear to be somewhat

more refractory than cones in the lime-kaolin system, owing probably to a higher viscosity of the liquid phase in the magnesia-kaolin system. The data of Rieke⁴⁹ indicate that, up to about 12 percent lime in a lime-kaolin mixture, the cone-deformation temperature is lowered about 45°F per percent of lime and that up to about 18 percent magnesia in a magnesia-kaolin system the cone-deformation temperature is lowered about 27°F per percent magnesia, which gives a ratio for the fluxing action of magnesia to the fluxing action of lime of 27/45, or 0.6. In general, a value for this ratio of 0.7 appears to be quite satisfactory over the range of silica to alumina ratios covered by coal ashes generally met with in the United States because as the ratio of silica to alumina changes from that of kaolin toward higher values the fluxing action of a given percentage of magnesia increases more rapidly than that of a comparable percentage of lime, as an inspection of the equilibrium diagrams shows.

Mazzetti⁵³ investigated the ash of a number of Italian lignites, reaching the conclusion that the ratio of the sum of alumina plus silica to the sum of lime plus magnesia plus ferric oxide could not be used as an index of fusibility. This is in accord with the data already presented.

Murray⁵⁴ stated that the softening temperature of the ash increased with decreasing sulfur content of the coal. This is only the crudest kind of approximation; it is based on the assumptions that sulfur can be used as an index of the iron content of the ash and that an ash of higher ferric oxide content will always have a lower softening temperature than one of lower ferric oxide content.

⁵² Lefebvre, H., and Boulant, P., *Compt. rend. 17me Congr. chim. ind.*, Paris, Sept.-Oct., 1937, pp. 1170-8.

⁵³ Mazzetti, C., *Ann. chim. applicata*, **20**, 3-17 (1930).

⁵⁴ Murray, J. A., *Power*, **59**, 561 (1924).

Schulze⁵⁵ stressed the effect of the mineralogical as well as the chemical composition of the ash; he stated that ferric oxide and lime increased the fusibility of the ash with the production of a vitreous pasty slag. These conclusions are in qualitative agreement with the fundamental theoretical background of the subject.

Staemmler,⁵⁶ utilizing the method of Bunte and Baum, investigated the effect of mixing lime, iron oxides, and silica in the form of various salts. His principal observation was that the addition of calcium as the sulfate had the effect of giving softening temperatures which differed from those obtained when calcium was added as the carbonate. Mixtures of lime and ferric oxide in proportions ranging from 0.5 to 2.0 moles of lime to 1 mole of ferric oxide softened from 30 to 40° C higher when lime was added as the sulfate than when it was added as the carbonate. On the other hand, and silica in proportions ranging from 0.5 to 1.0 mole of lime to 1.0 mole of silica softened from 60 to 70° C higher when lime was added as the sulfate than when it was added as the carbonate. Mixtures of lime and, when the composition range was 1.5 to 2.0 moles of lime to 1.0 mole of silica, the use of sulfates resulted in softening temperatures from 80 to 90° C lower than those obtained from corresponding mixtures when lime was added as the carbonate.

Staemmler reported that ignition at 1,200° C of lignite ash showing an original sulfate content of 34 percent resulted in the loss of only 9 to 12 percent sulfur trioxide in 90 minutes. This observation together with his other data indicate that coals containing large amounts of sulfates among their ash-forming mineral components might be expected to give ashes

which would deviate from the behavior predicted on the assumption that the ash behaves in fusing like a kaolin contaminated with basic oxides. Such ashes are very rare in the United States, and it is unlikely that any would be met with that contained sufficient sulfate sulfur to invalidate seriously the theoretical considerations previously discussed. Staemmler stated that, in the ternary system $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$, the addition of lime as sulfate effected an increase in softening temperature over that obtained when lime was added as carbonate only in instances in which the lime content of the fritted mass exceeded 25 percent. An ash having a lime content exceeding 25 percent of its lime plus silica plus ferric oxide content would be an extreme rarity in coals of the United States.

Winter and Mönnig⁵⁷ investigated the fusion points of ash from different structural parts of the Sonnenschein Seam by the methods of Bunte and Baum and of Dolch and Pöschmüller. They found that, in all samples, as the composition of the ash approached that of pure kaolin, the softening temperature increased. This is in strict agreement with the fundamental theoretical background of the subject.

Palmenberg⁵⁸ has shown that a very close correlation exists between the softening temperature of ash from Pennsylvania anthracite and the ratio of ferric oxide to the sum of alumina plus silica. Examination of Palmenberg's data shows that the ashes with which he worked contained very small and quite constant amounts of alkaline-earth oxides and that the alumina to silica ratio of the ashes was remarkably constant. These conditions constitute a special case within the theoretical considerations previously outlined, and the cor-

⁵⁷ Winter, H., and Mönnig, H., *Glückauf*, **67**, 156-60 (1931).

⁵⁸ Palmenberg, O. W., *Ind. Eng. Chem.*, **31**, 1058-9 (1939).

⁵⁵ Schulze, R., *Wärme*, **54**, 81-5 (1931).

⁵⁶ Staemmler, C., *Chem.-Ztg.*, **55**, 59-60 (1931).

relation obtained is to be anticipated from them.

Quantitative Correlations Between Fusibility and Chemical Composition. Probably the earliest attempt at correlating the composition of coal ashes with their fusibility was that of Prost,⁵⁹ who determined what he called the fusing temperature of 23 Belgian coal ashes and compared the temperatures for several ashes with the refractory quotient:

$$Q = \frac{\frac{\text{O in Al}_2\text{O}_3}{\text{O in CaO} + \text{O in Fe}_2\text{O}_3 + \text{O in MgO}}}{\frac{\text{O in SiO}_2}{\text{O in Al}_2\text{O}_3}}$$

He found that, in general, the fusing temperature increased with increasing values of Q but that there were several exceptions, notably ashes of high iron content.

De Graaf⁶⁰ gave curves purporting to show the effect of silica, ferric oxide, and sulfur on the fusion temperature as determined by the micropyrometer method, but his data were too meagre to justify his generalizations, which would not apply to a wide range of coal samples.

Nicholls and Selvig¹⁰ plotted the ferric oxide content of 43 ashes against their softening temperatures and showed that errors of several hundred degrees would often be made in predicting the softening temperatures from the curve showing the average variation in softening temperature with ferric oxide content for the group. It is interesting, however, to note that the ashes distributed themselves symmetrically around a line showing an average lowering in softening temperature of 41° F per percent ferric oxide.

Nicholls and Selvig also plotted the ratio:

$$\frac{\text{Al}_2\text{O}_3 + \text{SiO}_2}{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{N}} \div \text{K}_2\text{O}$$

against the softening temperature for the same 43 ashes. Although some of the points miss the average curve by as much as 300° F, there is a distinctly better correlation between R and the softening temperature than between the percentage of ferric oxide and the softening temperature.

Estep, Seltz, Bunker, and Strickler⁶¹ assumed that coal ash can be regarded as a four-component system SiO_2 - Al_2O_3 - Fe_2O_3 - CaO , and they expressed the composition of the ash by means of sections through a triangular prism at various percentages of lime which yield ternary diagrams expressing the composition of the ash in terms of the relative amounts of silica, alumina, and ferric oxide on the basis

$$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = 100 \text{ percent}$$

To estimate the softening temperatures it would, in theory, be necessary to have available sections through the triangular prism at levels corresponding to 1 percent or possibly 0.5 percent increments in lime content on which would be drawn softening-temperature isotherms, that is, lines passing through all points representing compositions having the same softening temperature. However, the authors stated that increments of lime up to 2.5 percent did not produce very large reductions in the softening temperature, and that, therefore, a single diagram representing the average of all sections from $\text{CaO} = 0.0$ percent to $\text{CaO} = 2.5$ percent might be used. This diagram they referred to as the "base ternary." For lime contents in excess of 2.5 percent the authors gave five additional ternary diagrams as follows:

⁶¹ Estep, T. G., Seltz, H., Bunker, H. L., Jr., and Strickler, H. S., *Mining and Met. Investigations, Carnegie Inst. Tech. and Mining and Met. Advisory Boards, Coöp. Bull.* 62 (1934), 47 pp.

⁵⁹ Prost, E., *Colliery Guardian*, 74, 602 (1897).

⁶⁰ De Graaf, G. A., *Coal Age*, 19, 534-9 (1921).

CALCIUM LEVEL PERCENT CAO

I	2.6 to 3.5
II	3.6 to 4.5
III	4.6 to 5.5
IV	5.6 to 6.5
VI	7.6 to 8.5

Calcium level V is omitted because the authors did not have sufficient data on ashes with a lime content in the range of 6.6 to 7.5 percent to permit construction of a ternary plot for this level. They compensated for this by presenting diagrams showing vertical planes through the prism which give plots of lime versus ferric oxide at constant silica-alumina ratios. On these planes were drawn softening-temperature isotherms, and by means of them softening temperatures could be estimated from the composition expressed in the manner described above.

The authors also described an alternative correlation which permitted the use of rectangular coordinates. This procedure, however, requires the unjustified assumption that the fluxing actions of lime and ferric oxide are identical. The fluxing action of lime on kaolin-silica mixtures averages from 35 to 50° F per percent depending on the silica to alumina ratio of the mixture, and there are ranges of composition where the fluxing action of lime is as high as 80° F per percent, as is shown in Figs. 3 and 5. The maximum fluxing effect of ferric oxide on a kaolin-silica mixture is about 30° F per percent, and its fluxing action decreases with additions of lime to the mixture except in certain limited regions in which it rises to as much as 40° F per percent. These regions are the composition ranges in the proportions of lime, alumina, and silica such that, in the absence of ferric oxide, the softening temperatures would be between 2,600 and 2,800° F. In these regions an increase in ferric oxide content from 5 to 15 percent

will effect reductions in softening temperature of 300 to 400° F.

There appears to be no advantage in the use of the rectangular plot. Since the basic assumption is that the ash can be treated as if its components were silica, alumina, and the sum of lime plus ferric oxide, the compositions might more readily have been expressed by means of the conventional triaxial coordinate system, but the authors felt that a two-dimensional plot was more concise and less unwieldy than any three-dimensional plot. They applied their "prism" correlation to 196 ash samples, 14 of which were ashes of coals as received. The remainder were obtained by mixing pairs of these coals in varying proportions. A statistical treatment of the deviations of their calculated softening temperatures from the corresponding measured values, when their more precise prism plots were used for estimation, yielded the data of Table IV.

TABLE IV

DISTRIBUTION OF DEVIATIONS

Magnitude of Deviation	Percent
Greater than 300° F	0.0
205 to 300	0.0
105 to 200	9.7
55 to 100	11.2
0 to 50	24.6
0 to -50	21.4
-55 to -100	21.4
-105 to -200	10.7
-205 to -300	0.5
Greater than -300° F	0.5

Percentage of deviations within $\pm 100^\circ \text{F}$ = 78.6.
 Algebraic mean of the deviations = -12.7°F .
 Average deviation of a single estimate = 66°F .
 Probable error of a single estimate = 56°F .

Since the allowable variation for a single observer using the A.S.T.M. standard method for determining softening temperatures is 50° F, the correlation appears to

be rather good. However, the negative value of the algebraic mean indicates that the correlation tends to yield calculated results which are, on the whole, lower than the corresponding observations. This may be regarded as preferable to a correlation tending to give high results.

However, the foregoing observations represent only a statistical test of the consistency of the correlation with data obtained in the laboratory which is responsible for making the correlation. To make an adequate test of the correlation it is necessary to apply it to data from some other source. In order to do this the writer has calculated the softening temperatures of 178 coal ashes using the prism plots. Of these 178 samples, 61 were taken from the data of Nicholls and Selvig.¹⁰ The remaining 117 samples represented analyses and softening temperatures from various coal-testing laboratories. The distribution of deviations calculated from observed results is shown in Table V.

TABLE V

DISTRIBUTION OF DEVIATIONS

Magnitude of Deviation	Data of U. S. Bur. Mines	All Other Data
	percent	percent
Greater than 300° F	0.0	1.2
205 to 300	0.0	2.3
105 to 200	5.5	16.1
55 to 100	5.5	10.3
0 to 50	29.0	17.2
0 to -50	40.0	12.6
-55 to -100	10.9	19.5
-105 to -200	9.1	16.1
-205 to -300	0.0	1.2
Greater than -300° F	0.0	3.5
Percentage within ±100° F	85.4	59.6
Algebraic mean	-10.7° F	-68.3° F
Average deviation	52° F	162° F
Probable error	44° F	137° F

The distribution in the Bureau of Mines data shows a closer correlation between observed and calculated results than the authors obtained with their own data. On the other hand, the correlation obtained with the data from miscellaneous sources is much poorer. The obvious inference is that the correlation of Estep et al. is, on the average, a more reliable index of ash-softening temperature than an actual measurement if made by an average laboratory chosen at random.

So much has been said in the past about the impossibility of calculating ash-softening temperatures from ash analyses that it is unlikely that this conclusion will be accepted without supporting evidence. In defense of the point of view and in support of the adequacy of the correlation to permit the calculation of ash-softening temperatures, within limits, data are submitted, in Table VI, showing the distribution of deviations obtained when a method of correlation based on the fundamental

TABLE VI

DISTRIBUTION OF DEVIATIONS

Magnitude of Deviation	Data of U. S. Bur. Mines	All Other Data
	percent	percent
Greater than 300° F	0.0	4.8
205 to 300	0.0	1.9
105 to 200	0.0	7.6
55 to 100	14.7	15.3
0 to 50	39.3	20.0
0 to -50	37.8	26.7
-55 to -100	8.2	11.4
-105 to -200	0.0	2.9
-205 to -300	0.0	3.8
Greater than -300	0.0	5.7
Percentage within ±100° F	100.0	73.4
Algebraic mean	3.3° F	3.6° F
Average deviation	37° F	100° F
Probable error	31° F	85° F

theoretical considerations presented and discussed in the first section of this part of the survey and supplemented by measurements on a large number of synthetic mixtures and coal ashes is applied to the same data.

The distribution of deviations obtained by applying this correlation to these data is quite similar to that which resulted from the application of the method of Estep et al. to the same data. If it is kept in mind that the two methods of correlation were independently arrived at from two different viewpoints and that both methods show a rather close correlation with the measured values presented by Nicholls and Selvig¹⁰ it is apparent that the measured softening temperature is rather closely determined by the chemical composition of the ash and it may be concluded that, with thoroughly reliable data, calculations made by the method of Estep et al. will agree with observations to within the tolerance for different laboratories for about four out of every five samples.

On the whole the agreement is remarkably good in view of the fact that the authors made the rather drastic simplifying assumption that coal ash can be regarded as a four-component system. It is true that graphical representation of a system of more than four components is very cumbersome, but a somewhat closer correlation may be obtained by taking account of additional components, without sacrificing the relative simplicity of four components, by assuming certain equivalences. Such assumptions are not altogether sound theoretically, but the errors introduced by them appear to be smaller, in practice, than those which result simply from neglecting the additional components.

The major components not accounted for in the method are titania, phosphorus pent-

oxide, magnesia, and the oxides of potassium and sodium. In the average ash analysis, titania and phosphorus pentoxide are not separately determined and are reported as alumina. This is unfortunate since, in most ashes (specifically those whose compositions on the basis lime plus alumina plus silica equals 100 percent lie in the field of mullite or of corundum), increments in alumina raise the softening temperature. Examination of the equilibrium diagram of the system $\text{TiO}_2\text{-Al}_2\text{O}_3$ shows that the behavior of titania is very similar to that of silica. In the system $\text{SiO}_2\text{-Al}_2\text{O}_3$ there is a eutectic at 95 percent silica with a melting temperature of $1,545^\circ\text{C}$ ($2,749^\circ\text{F}$). In the system $\text{TiO}_2\text{-Al}_2\text{O}_3$ the eutectic is at 80 percent titania and its melting temperature is $1,715^\circ\text{C}$ ($3,055^\circ\text{F}$). Since the percentage of titania in most ashes is usually around 2 to 3 percent and seldom exceeds 5 percent it appears to be desirable to assume an equivalence of silica and titania for the purpose of estimating ash-softening temperatures.

Phosphorus pentoxide would not remain uncombined in a coal-ash system at the temperatures involved, but it probably exists as calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$). Since it is an acidic oxide it should produce a fluxing action on the basic oxides present, but since it is chemically combined to form a rather stable compound of high melting point ($1,230^\circ\text{C}$, $2,182^\circ\text{F}$) its effect should be rather small. Apparently no serious discrepancy is involved in assuming it to be equivalent to additional silica.

To neglect titania and phosphorus pentoxide will not greatly affect predictions based on the chemical composition of the ash, but neglect of the basic oxides, particularly the oxides of potassium and sodium, is more significant. Estep and his co-workers recognized this, and in a later pub-

lication⁶² the effects of sodium oxide, lime, and magnesia were studied and compared.

In making this study the authors demonstrated that natural coal ashes and ashes synthesized from kaolin, silicic acid, calcium carbonate (or sulfate), and magnesia gave softening temperatures in substantial agreement. They concluded: (1) that the softening temperatures of natural ashes can be duplicated with synthetic ashes of similar composition; (2) that a satisfactory correlation can be arrived at by considering the ash as a four-component system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3\text{-CaO}$; (3) that the presence of alkali should be corrected for by reducing the calculated softening temperature by 50°F for each percent of sodium oxide; (4) that the lime-softening temperature relationship is practically linear up to 5 percent lime with a slope 50°F per percent; (5) that beyond 5 percent lime further study with synthetic mixtures is needed to establish the relationship and that the effect of magnesia is identical with that of lime up to 10 percent magnesia, therefore the sum of the two can be regarded as a single variable.

The first conclusion is in accord with the theoretical discussion which prefaced this part of the survey, but it would be safer to limit the generalization to ashes in which alumina is present primarily as a constituent of kaolin.

The second conclusion is demonstrated to be valid, within limits, by the data submitted by the authors provided that corrections for magnesia and alkali oxide are made.

Conclusions 3, 4, and 5 merit a more detailed consideration. Conclusion 4 indicates that the authors believed that addi-

tional data are needed to establish the effect of lime in excess of 5 percent. It will be observed from the data given in Figs. 3, 4, and 5 that, if they had based their correlation on a prism for which the base ternary was the lime-alumina-silica system for which a phase-equilibrium diagram was available instead of on one in which the base ternary was the ferric oxide-alumina-silica system for which equilibrium data are not available, the necessity for determining more points might have been obviated.

The existence of minima in curves showing the effect of increments of lime on the softening temperatures of coal ashes is to be anticipated, as Fig. 3 shows. Examination of this figure indicates that additions of lime to any mixture the composition of which lies in the field of mullite will lower the softening temperature of the mixture until the composition of the mixture plus lime reaches the mullite-anorthite phase boundary. At this point there will be a minimum in the curve, and further additions of lime will raise the softening temperature provided that the silica to alumina ratio is not too large. It may be seen from Fig. 3 that, as the ratio of silica to alumina approaches the value 3.5 (which is the silica to alumina ratio at the ternary eutectic between mullite, anorthite, and cristobalite [melting temperature $2,453^\circ\text{F}$]), increases in lime content beyond the amount necessary to reach the mullite-anorthite phase boundary will produce smaller and smaller increases in softening temperature. In fact, after the silica to alumina ratio passes the value 2.1, crossing the phase boundary by the addition of lime results in only a very small rise which continues up to about 20 percent lime (the approximate lime content of anorthite), after which further additions of

⁶² Estep, T. G., Seltz, H., and Osborn, W. J., *Mining and Met. Investigations, Carnegie Inst. Tech., Mining and Met. Advisory Boards, Coöper. Bull.* 74 (1937), 18 pp.

lime again produce a lowering in softening temperature.

The correctness of these generalizations based on the equilibrium diagram for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system is confirmed by the data of Zvanut and Wilson,⁶³ who determined pyrometric cone equivalents for the system lime-alumina-silica. The data of Zvanut and Wilson cannot be applied directly to coal-ash systems because of differences in test method and degree of deformation taken as the end point, but, if due allowance is made for these differences, their data are in complete agreement with the generalizations above.

Equilibrium diagrams for the systems $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ in the regions including the composition ranges of coal ashes are not available. The data of Kracek⁶⁴ on the effect of alkali and alkaline-earth oxides on cristobalite indicate very similar slopes for the liquidus curves of the $\text{Na}_2\text{O-SiO}_2$, $\text{K}_2\text{O-SiO}_2$, CaO-SiO_2 , and MgO-SiO_2 systems. Both the CaO-SiO_2 and the MgO-SiO_2 systems show a wide range of compositions over which there is no change in the liquidus temperature due to the formation of immiscible liquids, which would suggest that lime and magnesia would be less active fluxes than the alkali oxides, but the ternary diagrams for the systems $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ show that the introduction of alumina results in a very small immiscible liquid region in the ternary systems. Consequently it would appear justifiable, until more data are available, to assume substantially equivalent fluxing action by all the alkaline-earth and alkali oxides. It will be observed that the assumption of equivalence in fluxing action between mag-

nesia and lime is inconsistent with the data of Rieke⁴⁹ on kaolin, to which reference was made earlier, but the data of Estep, Seltz, and Osborn appear to be quite incontrovertible and were, moreover, determined under the conditions of the A.S.T.M. standard method, which Rieke's were not.

It is unfortunate that these authors did not investigate the effect of substituting alkali oxide for lime in the same way as was done for magnesia, as it is certainly simpler to include the sum of the alkaline-earth and alkali oxides as one component, although no objection can be raised to their procedure of subtracting 50° F per percent alkali oxide from the calculated temperature, which is not quite equivalent to the procedure of adding the alkali oxide to the alkaline-earth oxide before making the calculation. In fact, in the absence of experimental evidence as to equivalence of fluxing action, it is, perhaps, a more justifiable procedure to treat alkali oxide as a separate component although its inclusion with the alkaline earth has been found to give satisfactory results.

It must be recognized that there are limits to the accuracy of any practically workable procedure of this kind. For example, the observation that magnesia can often be treated as equivalent to lime in many instances does not prove that it can always be so treated. With thoroughly reliable data, a method of correlation such as that of Estep and his coworkers should give calculated softening temperatures that agree with measured softening temperatures, within the allowable tolerance for different laboratories (90° F), about nine times out of ten.

Moody and Langan⁶⁵ have described a correlation similar to that of Estep and his coworkers in that they chose to plot

⁶³ Zvanut, F., and Wilson, H., *J. Am. Ceram. Soc.*, **17**, 255-6 (1934).

⁶⁴ Kracek, F. C., *Ann. Rept. Dir. Geophys. Lab. Yearbook* **32**, 61 (1932-3).

⁶⁵ Moody, A. H., and Langan, D. D., Jr., *Combustion*, **6**, No. 8, 13-20 (1935).

isotherms in planes parallel to the ferric oxide-alumina-silica base. However, they preferred the conventional regular tetrahedron for expressing the compositions diagrammatically. As the fourth component they plotted lime plus magnesia. Their original publication gave isotherms only for the level $\text{CaO} + \text{MgO} = 5$ percent. These were obtained from softening-temperature measurements on synthetic mixtures of kaolin, silica, ferric oxide, and dolomite. In addition to giving softening temperature-composition data, Moody and Langan presented a diagram giving initial deformation temperatures as a function of composition.

The composition range covered by the diagrams of Moody and Langan was greater, with reference to the proportions of ferric oxide, alumina, and silica, than that covered by the diagrams of Estep and his coworkers, but, since Moody's and Langan's data applied only to one lime plus magnesia level, they appear to be of limited usefulness. With reference to this the authors stated:

The data for softening temperatures used in the construction of Fig. 8 [their softening temperature-composition diagram] agree in general with a limited chart recently made by Estep et al. from coal-ash analyses showing about 5 percent calcium oxide. The latter chart does not cover as wide an area of composition as Fig. 8 and hence does not show the influence of surrounding areas. Other charts from their data indicate that the content of lime from 2.5 percent to 8.5 percent changes the fusion temperature less than 100°F in most cases.

Reference to Fig. 5 indicates that Moody and Langan have underestimated the effect of lime. This quotation is the only reference to the reliability of their diagrams, as they gave no supporting data. Their paper includes an excellent theoretical discussion of coal-ash fusibility and

some interesting data on the effect of furnace atmosphere on the initial deformation temperatures and softening temperatures of ashes of varying compositions.

Schaefer and Demorest⁶⁶ based their correlation on the idea that over the composition ranges of most coal ashes the liquidus curves for the systems involved may be approximated by straight lines. Having thus obtained liquidus curves of constant slope it is possible to compare these slopes and find factors relating the fluxing effect of the several basic oxides. Very briefly summarized, Schaefer's procedure is as follows: If the ash consists only of alumina and silica, then the softening temperature (S.T.) would be described by an equation of the form

$$\text{S.T.} = f(\text{Al}_2\text{O}_3, \text{SiO}_2)$$

Moreover, for the composition range of coal ashes the liquidus curve can be approximated very closely by a straight line. Therefore the equation becomes

$$\text{S.T.} = k(\text{Al}_2\text{O}_3, \text{SiO}_2)$$

where k is the slope of the line. However, the softening temperature will be reduced by a factor depending on the ratio of the fluxes to the sum of the alumina plus silica present. Therefore the equation becomes

$$\text{S.T.} = k \frac{(\text{Al}_2\text{O}_3)}{(\text{SiO}_2)} \times f \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{FeO} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}$$

The problem then is to discover the form of the function

$$f\left(\frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{FeO} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}\right)$$

From the equilibrium diagrams for the lime-alumina-silica system Schaefer con-

⁶⁶ Schaefer, R. L., master's thesis (M5 S2943), The Ohio State University, 1933.

structured liquidus curves showing the effect of lime and magnesia on alumina-silica mixtures in which the ratio of silica to alumina is 1.5, a good average for coal ashes. He found that the curves so obtained could be approximated by straight lines of substantially equal slope. The approximation is rather poor for lime. Since the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems were not available he constructed a liquidus curve from the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system for compositions containing 5 percent lime. The straight line approximating this curve had substantially the same slope (per percent sodium oxide) as the lines for the effect of lime and magnesia on the alumina-silica mixtures. Therefore Schaefer concluded that the sum of the oxides of calcium, magnesium, sodium and potassium could be treated as a single variable.

Iron gave more trouble, but Schaefer decided that the fluxing action of lime averaged about six-tenths that of iron. Consequently his equation became

$$\text{S.T.} = f \left(\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} \times \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{FeO} + 0.6(\text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O})} \right)$$

Schaefer plotted the quantity

$$\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} \times \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{FeO} + 0.6(\text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O})}$$

against the softening temperature for 98 coal ashes, obtaining the curve shown in Fig. 7. An analysis of the data shows the following:

1. Of the 98 points 7 lie on the curve, 56 lie above the curve and 35 lie below the curve.

2. The average error for points above the curve is -53°F ; that for points below the curve, $+50^\circ\text{F}$. The average error regardless of sign is 48°F .

3. An error equal to or greater than 100°F occurred only 11 times.

On the whole the agreement between calculated and measured values is very good, better than it is for any other system

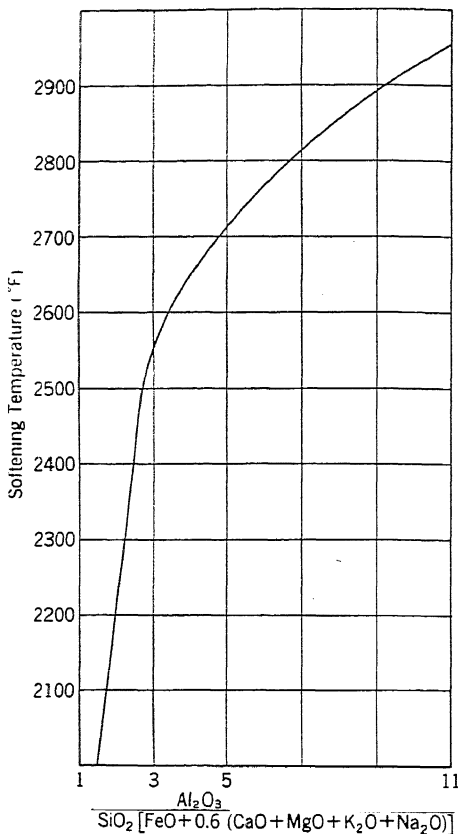


FIG. 7. Schaefer's correlation.**

of correlation with which the writer is familiar—better even than the assumptions on which the correlation is based would appear to justify one in expecting. This may be due to the rather small number of samples, which, perhaps, accounts also for the preponderance of negative over positive errors.

The straight lines which Schaefer derived

from the equilibrium diagrams showed an average fluxing action for the alkaline-earth and alkali oxides of only about 20° F per percent. The data of Estep, Seltz, and Osborn⁶² and the writer's experience indicate that, so far as an average can be obtained, it is nearer 30 than 20° F per percent for lime and magnesia. For sodium oxide the data of Estep, Seltz, and Osborn show an average of about 50° F per percent. It appears that Schaefer's curve of correlation should be tested with a larger number of ashes to establish its reliability with greater certainty.

Jones and Buller⁶⁷ suggested a simple approximate relationship between composition and softening temperature. They gave a curve, based on analyses and softening-temperature measurements for a number of anthracite ashes, which showed the reduction in softening temperature below the liquidus temperature of the Al_2O_3 - SiO_2 system by the sum of the basic oxides, including iron. For example, consider an ash having the following composition: SiO_2 , 40.4; Al_2O_3 , 38.6; Fe_2O_3 , 4.7; TiO_2 , 1.5; P_2O_5 , 4.0; CaO , 5.6; MgO , 0.5; Na_2O , 0.4; K_2O , 0.9; SO_3 , 2.6. The first step is to find the percentage of alumina in the mixture alumina plus silica. This is equal to $(38.6 \times 100)/79$, or 48.9. Referring to the alumina-silica equilibrium diagram it is found that this composition has a liquidus temperature of 1,800° C or 3,272° F. The sum of ferric oxide plus lime plus magnesia plus the oxides of sodium and potassium equals 12.1. From the curve for the lowering of the liquidus by the sum of the fluxes it is found that 12.1 percent of fluxes corresponds to a lowering of 290° F. Therefore the calculated softening temperature is 3,272 minus 290, or 2,982° F. The

measured softening temperature for this ash was 2,930° F.

The use of the alumina-silica liquidus as a reference line is, of course, theoretically sound, but the method makes two assumptions not justified by the facts. The first of these is the equivalence of all the basic oxides, including ferric oxide. Although there is good evidence that rather satisfactory results are obtained by assuming the equivalence of the alkaline-earth and alkali oxides the inclusion of ferric oxide is not justifiable, as has been pointed out earlier in this survey. The second assumption is that one curve suffices to describe the fluxing action of the fluxes over the entire range of silica-alumina ratios occurring in coal ashes. Reference to Figs. 3 and 5 shows that this is impossible. It should be remarked, however, that Jones and Buller were concerned, primarily, with the ash of Pennsylvania anthracite, which does not vary so widely in composition as the ashes of the various ranks of bituminous coals.

Thiessen, Ball, and Grotts⁶⁸ have stated that the fusion characteristics of coal ashes can be related to the equilibrium diagrams of the three ternary systems which make up the quaternary system CaO - Al_2O_3 - SiO_2 - Fe_2O_3 . However, as they do not indicate how this is done, only passing reference to their work is made here.

Summary. To sum up this section on the relationship between ash composition and ash-softening temperature it may be said that, for practical purposes, the ash may be treated as a four-component system of silica, alumina, basic oxides (CaO , MgO , K_2O , Na_2O), and ferric oxide (ferrous oxide is the major component under the test conditions, but this fact does not prevent the use of ferric oxide as an index),

⁶⁷ Jones, D. J., and Buller, E. L., *Ind. Eng. Chem., Anal. Ed.*, **8**, 25-27 (1936).

⁶⁸ Thiessen, G., Ball, C. G., and Grotts, P. E., *Ind. Eng. Chem.*, **28**, 355-61 (1936).

that the composition-softening temperature relationship is closely related to the phase equilibrium diagrams for the corresponding systems, and that the only published correlation supported by comparisons with actual data in sufficient quantity to justify its use is that of Estep and his coworkers.

The very considerable expenditure of time and effort by those who have endeavored to develop such relationships is justified by the usefulness of a reliable correlation in forming an estimate of the probable effect of mixing two coals on the softening temperature of the ash of the mixture.

ASH FUSIBILITY AS AN INDEX OF CLINKER TROUBLE

In view of the great mass of data that has been obtained on the fusibility of the ashes of individual coals and of the lively interest in methods of measuring ash fusibility it might be assumed that the fusibility of ash is a fairly reliable index of the clinker trouble to be anticipated. Actually the subject is highly controversial, with opinions varying from the extreme which almost makes a fetish of fusibility measurements as a reliable guide to the other extreme which regards them as all but futile. The circumstances leading to such widely diverse attitudes may be classified under four heads: (1) variations in the phenomena referred to as "clinker trouble"; (2) variations in the design and operation of the equipment in which the coal is burned; (3) variations in the coal as burned; (4) variations between operating conditions and test conditions.

No single laboratory test can be expected to serve as an index of such varied phenomena as the growth of large clinker in parts of a fuel bed, the adhesion of slag to refractory walls, the adhesion of

slag to grate bars or tuyères or the destruction of these metal parts by solution in slag components, and reduced output or complete shutdowns. Nicholls and Selvig¹⁰ have discussed this aspect of the subject, pointing out that there are no scales of measurement whereby these troubles may be quantified and correlated with a laboratory test.

It must also be apparent that a particular coal will behave quite differently according to the type of fuel bed in which it is burned. The underfeed stoker concentrates the ash, mixes it, holds it in regions of extreme temperature for prolonged periods, and, in general, exposes it to very high temperatures. The overfeed bed is less severe in its treatment of the ash, but, if the bed is hand-fired, the fireman may cause serious trouble by undue agitation of the bed, particularly if the coal cokes heavily. In the powdered-fuel furnace the whole idea of what is meant by clinkering must be revised. Indeed it is doubtful that the term can be applied at all, although phenomena attendant upon the fusion and flow of coal-ash slags are of vital importance.

Coal is a highly variable entity not only as regards the distribution and nature of its ash-forming mineral content but also in the composition and properties of the coal substance itself, particularly the coking properties, which may influence the fusion and flow of the ash. Gauger⁶⁹ in discussing this subject pointed out that Morrow and Proctor⁷⁰ obtained results indicating that variations in sampling the coal may lead to ash-softening-temperature determinations differing by as much as 500° F and

⁶⁹ Gauger, A. W., *Proc. Am. Soc. Testing Materials*, 37, Pt. II, 376-401 (1937).

⁷⁰ Morrow, J. B., and Proctor, C. P., *Trans. Am. Inst. Mining and Met. Engrs.*, 119, 227-69 (1936).

quoted Viall⁷¹ to the effect that at least 20 samples of commercial shipments of a given size are necessary to obtain a good approximation to the true average value for a particular coal. It would appear, under the circumstances, that a reliable average value is not an altogether satisfactory criterion of the day-to-day performance of the coal in the fuel bed. To some extent the significance of the average value will depend on whether or not the coal has been well prepared to remove sizable ash-forming mineral aggregates, but the best of preparation cannot eliminate the variable distribution of that portion of the ash-forming mineral matter which is so closely associated with the coal substance as to defy separation by preparation.

It has always been recognized that the A.S.T.M. standard method involves a set of conditions quite different from those that obtain in a fuel bed. The ash is liberated from the coal substance at a much lower temperature, it is ground and intimately mixed before being heated to the temperature range in which fusion occurs, and, most important of all, no segregation or removal of components is permitted to occur. Moreover, it is heated at a definite rate in an environment calculated to keep the iron in the ferrous state of oxidation, and there is no way in which the test can take account of the total ash content of the coal.

In a fuel bed the ash is liberated under variable temperature conditions, and the proportions of the components, as liberated, will differ greatly from the average. The fineness of subdivision and the intimacy of mixture obtained in making the test are not duplicated in the fuel bed, and marked segregation of the components occurs. The rate of heating is variable, and the oxidiz-

ing potential of the environment varies from point to point over wide limits. Moody and Langan⁶⁵ pointed out that they found clinkers from stoker-fired furnaces in which the iron was in the form of ferric oxide and, on the other hand, that large pieces of metallic iron had been found in the slag taken from the bottom of slagging-type furnaces. In another paper⁷² these authors submitted abundant evidence of the segregation of ash components which occurs in boiler furnaces.

Ricketts⁷³ has stated that, when coals from eastern Pennsylvania and from West Virginia are burned on large underfeed stokers, only about 60 percent of the ash passes to the ashpit by way of the extension grate, the remaining 40 percent being lifted from the fuel bed by the draft. Some of this ash, which is carried out of the fuel bed in a molten or semimolten condition, adheres to the side walls of the furnace, some adheres to the tubes, and some, about 25 percent of all the ash in the coal, passes between the tubes and is either caught back of the bridge wall in the flues or passes out the stack. He pointed out that the ash may contain up to 60 percent of unburned carbon, a condition which does not exist when the softening temperature is measured. Ricketts summarized his knowledge of the relation between ash-fusion temperatures and clinker trouble as follows:

1. With coal from the same bed the clinker trouble usually increases as the fusion temperature decreases.
2. With coals from the same bed clinker trouble usually increases with an increase in ash content.
3. With coals from different beds the relation between ash-fusion temperatures and clinker trouble may vary through fairly wide

⁷¹ Private communication from S. H. Viall to A. W. Gauger.

⁷² Moody, A. H., and Langan, D. D., Jr., *Combustion*, 5, No. 4, 15-7 (1933).

⁷³ See p. 68 et seq. of ref. 10.

limits. This characteristic is well illustrated by a comparison of the coals from the eastern Pennsylvania fields with those from the Pocahontas and New River districts of West Virginia. The writer has seldom seen a coal from Pennsylvania with a fusion temperature below 2,450° F which did not give serious clinker trouble. Few of the coals from West Virginia have an ash fusion point above 2,450°; many of these coals with a fusion point between 2,200° and 2,300° have given little or no trouble from clinkers. The reason for this difference in performance is one of the many points which are not understood in the clinker problem.

The observations of Ricketts, when considered in conjunction with the differences which, on the average, exist between the ash composition of coals from the eastern Pennsylvania fields and those from the Pocahontas and New River regions of West Virginia, constitute the key to a more complete understanding of certain aspects of the clinkering problem. However, it will be preferable to defer consideration of this matter until the viscosity and surface tension of coal-ash slags have been discussed later in this survey.

In spite of the mass of evidence that may be adduced to demonstrate the inadequacy of ash-fusion measurements as a guide in predicting various types of clinker trouble, it would be unwise to reject the method of test or even to regard cone-fusion determinations as of negligible significance, as Gauger⁶⁹ has suggested. So long as coal is burned on grates it is probable that the perspicacious operating engineer will be able to derive benefit from cone fusion determinations by the application of a set of empirical rules, like those of Ricketts quoted above, devised to meet his particular operating conditions. That cone-fusion measurements can be related at least qualitatively to some of the phenomena involved is demonstrated by the

work of Nicholls, Corban, and Alderman⁷⁴ and by Nicholls and Selvig,¹⁰ who demonstrated a rough agreement between clinker size and ash-softening temperature, and by its utilization by Fehling in a theoretical investigation of the slagging of refractories which will be discussed later in this survey.

The behavior of molten slag on cooling may be of greater significance in the operation of large equipment at high ratings than what happens when pulverized ash is heated, and a method of test calculated to throw light on slag behavior will be suggested later in a section of this survey dealing with the flow of slags at temperatures below the liquidus. Nevertheless, it appears probable that cone-fusion determinations will continue to be used as a guide because of the care with which the procedure has been worked out and because of the relative simplicity of the method. However, modifications calculated to indicate the magnitude of the variations due to segregation of ash components during firing and in the fuel bed will perhaps be introduced. In this connection attention is directed to a paper by Gould and Brunjes⁷⁵ which presents important data on variations in fusibility of the ash from physically separable portions of the coal.

On the other hand, if the trend away from fuel beds to pulverized-fuel furnaces continues, there can be little doubt that methods of investigation will be developed calculated to provide information particularly adapted to the problems arising with this type of equipment. Some proposals have already been made, particularly by Bailey, and they will be discussed later in consideration of the problem of tube slagging.

⁷⁴ Nicholls, P., Corban, C. L., and Alderman, C. L., *Proc. Am. Gas Assoc.*, 1929, 1068-79.

⁷⁵ Gould, G. B., and Brunjes, H. L., *Trans. Am. Inst. Mining Met. Engrs.*, 139, 364-75 (1940).

It is apparent that no single property of an ash can be taken as an index of such varied phenomena as size of clinker, adhesion to grate bars on tuyères, slagging of refractories, tube slagging, and loss of combustible matter in the ash. If the maximum fuel-bed temperature to which the ash is exposed for considerable lengths of time is considerably below the softening temperature of the ash, it is unlikely that large, dense, vitreous clinker will form and the probability of serious adhesion to grate bars or tuyères is small. If the maximum fuel-bed temperature to which the ash is exposed for considerable lengths of time is considerably in excess of the softening temperature of the ash, the phenomena occurring will depend primarily on the properties of the fluid slag produced by fusion of the ash in relation to the design of the burning equipment and the operating technique.

THE VISCOSITY AND SURFACE TENSION OF COAL-ASH SLAGS

Nearly all who have studied the fusibility of coal ash in connection with clinkering and related problems have appreciated the important role played by viscosity in determining behavior of the molten slag, and this property of the fused ash is frequently mentioned in publications. The significance of surface tension of the slag, however, appears not to have been appreciated, judging by the scarcity of references to this property. This is rather surprising since the first step in grate-bar erosion and slagging of refractories is the wetting of the solid surface by the liquid, a phenomenon controlled primarily by surface forces.

The practical difficulties involved in the measurement of coal-ash slag viscosity are due primarily to the considerable amounts of iron oxides contained in substantially all

coal ashes. Their presence introduces a serious problem in the selection of a material for a container to hold the slag during measurements. Were iron not present, graphite containers could be used, as indeed they have been for blast-furnace slags. The presence of iron oxides makes it impossible to use graphite for the obvious reason that the oxides would be reduced rapidly to metallic iron with a resultant change in composition and properties of the slag with time. The investigator, therefore, must choose between a container made from some refractory material or one made from platinum or a platinum alloy. If he chooses, say, a porcelain body, the basic oxides will flux the container and the composition of the slag will slowly change as the result of the solution. If the slag has a very high basic oxide content, the fluxing action may be quite rapid at the higher temperatures and destruction of part of the apparatus and change of composition may ensue. If platinum is chosen the iron oxides in the slag will attack it, and the effect will be accentuated in a reducing environment. Consequently the use of platinum for such purposes becomes inordinately expensive.

One very vexing aspect of the problem may be illustrated by reference to Fig. 2. Curve 1 is the liquidus curve for the system; that is, it is the locus of all points such that an infinitesimal increment in temperature will cause the disappearance of the solid phase. If a mixture of 50 percent silica and 50 percent ferrous oxide is heated under reducing conditions to a temperature in excess of 2,970° F (the liquidus temperature for this composition), there will be obtained, upon reaching equilibrium, a homogeneous liquid phase which will have a viscosity characteristic of the composition and the temperature. However, if the temperature is lowered to 2,800°, cristo-

balite will crystallize from solution to an extent depending only on the composition and the temperature. For the conditions chosen the mixture will consist of about 91 percent liquid and 9 percent solid.

As a consequence of these circumstances two facts are at once apparent: (1) the mixture will continue to flow; and (2) the term viscosity no longer has a precise meaning. To be sure, if the liquid could be separated from the solid phase it would have a viscosity characteristic of its composition and temperature. As a matter of fact, the viscosity of the pure liquid phase can be measured because its composition is known from the liquidus curve itself. The liquidus curve tells us that at 2,800° F the composition of the liquid which is in equilibrium with the cristobalite that crystallized from a melt originally containing equal weights of silica and ferrous oxide is given by the point X; that is, the composition of the liquid is silica 45 percent, ferrous oxide 55 percent. Therefore we could, if we wished, make a melt of this composition and measure its viscosity over a temperature range from, say, 3,000° to 2,810° and extrapolate to 2,800°, thereby avoiding the possibility of separation of a solid phase during measurement.

However, such an artifice would not be instructive for the purpose in hand, which is to devise a means for characterizing the flow of a 50-50 mixture of silica and ferrous oxide at 2,800° F. It is apparent, moreover, that this problem continues to exist at all temperatures down to 2,156° F, the eutectic isotherm of the system. At this temperature, or more properly speaking at a temperature infinitesimally above it, the percentage of liquid in the mixture is given by $(50 \times 100)/62$, which equals 80.6 percent. This indicates that unless the liquid were very viscous indeed, which it is not, the mixture would continue to flow unless

it were held at this temperature long enough for the crystals of tridymite to grow until they formed an interlocking network, under which conditions, if the crystalline network were subjected to a mechanical constraint while the liquid was free to flow under gravity, the liquid phase would drain away from the solid phase. Of course, if the temperature is adjusted to a value infinitesimally below the eutectic isotherm, tridymite and fayalite will crystallize together from the melt in proportions dependent only on the composition of the batch and the liquid phase will disappear.

The foregoing discussion is based on the assumption that the system reaches equilibrium under the conditions of measurement. Frequently, however, and particularly if the composition of the slag is such that the liquid phase is very viscous, the system will not reach equilibrium for many hours after a given set of conditions has been established. This is especially true if the temperature is changed rapidly over a considerable interval. Consequently, if the temperature is raised rapidly from some value below the liquidus to a value above it, a solid phase may persist for many hours, making correct measurements of viscosity impossible. Conversely, if the system is at a temperature above the liquidus, a lowering in temperature to a value well below the liquidus may not result in the separation of any solid phase. When this happens it is possible to measure viscosities over a range of temperatures above and below the liquidus and obtain a smooth curve for the viscosity-temperature relationship which shows no abnormal change in slope at the liquidus temperature.

It may be remarked in passing that measurements made on a slag that does not readily devitrify (that is, separate a solid, crystalline phase) at temperatures

below the liquidus are of great significance in connection with the practical problems of removing ash from slag-tap furnaces and of clinkering. It will be shown later in this survey that slags having compositions such that they do not readily devitrify are, in general, desirable from the point of view of the operator of a slag-tap furnace and, in general, undesirable from the point of view of the operator of a furnace which burns coal on grates in which clinker troubles are likely to occur.

Another practical problem confronting the investigator of viscosity-temperature relationships of coal-ash slags is presented by the fact that iron may exist in three states of valence. Reid⁷⁶ has shown how the degree of oxidation may be controlled and has investigated the effect of the state of oxidation of the iron on the flow temperatures of slags. Further reference to his work will be made.

A basic difficulty that enters into studies of viscosity-temperature relationships in multicomponent systems is that there is no broad, fundamental theory of the relationship between viscosity and composition to guide the investigator. Earlier in this survey it was shown that the fusion-composition relationships could, in spite of the large number of components involved, in general be understood and predicted by reference to the phase-equilibrium diagrams for known systems of fewer components. The significance of equilibrium diagrams for the investigator of viscosity-temperature relationships of coal-ash slags has already been considered at some length, and it has been remarked that, because the phase rule provides information regarding systems in a state of equilibrium only, its applicability, even in a general way, is seriously proscribed when the system re-

quires many hours to attain equilibrium.

It is interesting to observe, however, that, at temperatures above the liquidus, the relationship between composition and viscosity appears to exhibit some correlation with the equilibrium diagrams. Herty and Hartgen and their coworkers⁷⁷ have investigated temperature-viscosity rela-

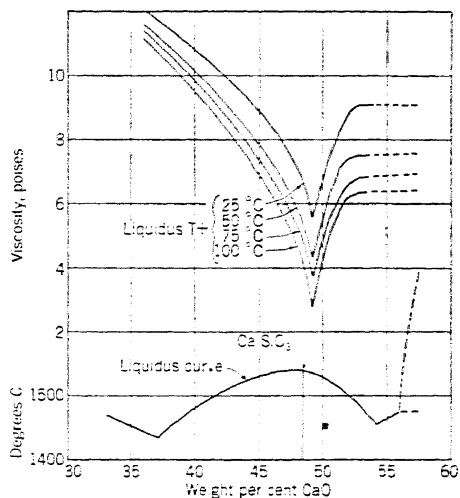


Fig. 8. Composition-viscosity curves for the lime-silica system data of Herty, Hartgen, et al.⁷⁷

tionships in the lime-silica system. In expressing their results they gave not only viscosity-composition isotherms, but also viscosity-composition curves for which temperatures are expressed, not in the customary manner as degrees above an arbitrary reference point, but as degrees above the liquidus curve of the system. The nature of this novel and interesting plot is shown in Fig. 8. Inspection of the figure immediately shows a pronounced minimum in viscosity in the vicinity of the compound

⁷⁶ Reid, W. T., *Ind. Eng. Chem., Anal. Ed.*, **7**, 835-8 (1935).

⁷⁷ Herty, C. H., Jr., Hartgen, F. A., Heidish, J. A., Metcalfe, K., Norris, F. G., and Royer, M. B., *Mining and Met. Investigations, U. S. Bur. Mines, Carnegie Inst. Tech., Mining and Met. Advisory Boards, Coop. Bull.* **47** (1930), 27 pp.

monocalcium silicate. Whether or not the curves would pass through maxima and then descend to new minima as the composition range was extended toward adjacent compounds cannot be concluded from the data. However, such behavior is suggested by the diagram. It is to be regretted that more plots of this type have not been made.

THE VISCOSITY OF COAL-ASH SLAGS IN THE ABSENCE OF A SOLID PHASE

With the exception of the work of Endell and Wens⁷⁸ and a paper by Endell, Wens, Rosin and Fehling,⁷⁹ the only investigation which has proceeded from practical and empirical beginnings to the development of a fundamentally sound procedure for the measurement of viscosity in absolute units is that made by Nicholls and his coworkers. This development is described in a series of four papers, one by Sherman, Nicholls, and Taylor,⁸⁰ and three by Nicholls and Reid,⁸¹ which constitute a set of progress reports for the American Society of Mechanical Engineers Special Research Committee on Removal of Ash as Molten Slag from Powdered-Coal Furnaces.

Considerations of space render it quite impossible adequately to discuss these papers in this survey. They contain a wealth of detail and should be read in their entirety. It will be possible only to indicate the methods used and the nature of the results obtained.

The first paper of the series described the results obtained in plant-scale tests made on three coals in two different boiler

furnaces at the Toronto, Ohio, station of the Pennsylvania-Ohio Power and Light Company. The boilers were designated as boiler 4 and boiler 5. The boiler and furnace installations were described in detail in the paper. The composition and fusibility of the ashes of the three coals fired are indicated in Table VII. Proximate and

TABLE VII

COMPOSITION AND FUSIBILITY OF ASH OF THREE COALS FIRED IN TESTS AT TORONTO, OHIO

Ash from	Strip Mine Coal	Pittsburgh Coal	Georges Creek Coal
Composition, percent			
SiO ₂	46.3	51.7	56.2
Al ₂ O ₃	24.4	26.9	33.5
Fe ₂ O ₃	23.8	10.6	5.4
CaO	1.7	3.9	1.1
MgO	0.8	0.8	0.6
Fusibility (°F)			
Initial deformation temperature	2,050	2,320	2,600
Softening temperature	2,180	2,470	2,700
Fluid temperature	2,400	2,640	2,790

ultimate analyses and sources of the coals are also given in the paper.

In making the tests care was taken to insure that only one coal was reaching the boiler. The temperature of the slag both at the tapping spout and in the slag bed was measured with a platinum, platinum-rhodium thermocouple. The furnace gases were sampled and analyzed for carbon dioxide, oxygen, carbon monoxide, hydrogen, and methane. Slag was sampled both at the spout and in the slag bed; it was analyzed, and fusibility determinations were made on it. The dust carried in the combustion gases was sampled and analyzed, and fusibility determinations were made on it.

⁷⁸ Endell, K., and Wens, C., *Glastech. Ber.*, **13**, 73-86 (1935).

⁷⁹ Endell, K., Wens, C., Rosin, P., and Fehling, R., *Angew. Chem.*, **48**, 76-9 (1935); *Z. Ver. deut. Chem., Beihefte* **12** (1935), 20 pp.

⁸⁰ Sherman, R. A., Nicholls, P., and Taylor, E., *Trans. Am. Soc. Mech. Eng.*, **51**, 399-413 (1929).

⁸¹ Nicholls, P., and Reid, W. T., *ibid.*, **54**, 167-90 (1932), **56**, 447-65 (1934), **62**, 141-53 (1940).

The authors investigated the condition of the slag in the hearth and the ease with which it could be tapped. They determined the combustible content of the slag samples. In one instance they took samples of slag at various depths from a bed of solidified slag, analyzed the samples, and determined their fusibility. As results they found that the iron content increased, the silica content decreased, and the softening temperature increased down to a depth of 12 inches. These data are important because they show that segregation of the ash components occurs in a large bed of molten slag. Consequently any tests made on a laboratory scale are inevitably limited in their applicability to the operation of slag-tap furnaces by the extent to which the segregation which occurs in full-scale operations shifts the composition of the slag from point to point. In this connection the segregation which occurs in the formation of fly ash is also significant.

Analyses were made of the gases near the surface of the slag bed. The authors felt that the number of samples analyzed was insufficient to permit the establishment of a reliable average value, but considerable amounts of carbon monoxide and hydrogen (as much as 9.5 and 5.4 percent, respectively, in one instance) were found in some of the samples, indicating that, at times, the atmosphere just above the bed might be strongly reducing.

The possibility of adding fluxes to the ash to increase the ease of tapping was considered, and the effect of adding ferric oxide to the ash of the Pittsburgh coal on the softening and fluid temperatures was investigated. This showed that the addition of 10 percent ferric oxide lowered the fluid temperature to a point where it appeared that the slag might be tapped without difficulty.

In summarizing their observations the authors pointed out that:

1. A selective separation of the ash components, which increased the proportion of ferric oxide in the slag compared to that in coal ash, occurred with all the coals.

2. The slags showed lower softening temperatures than the corresponding ashes.

3. The percentage of the ash passing to the stack increased with increasing fluid temperature of the original ash.

4. For similar coals, slagging-bottom operation decreased the percentage of ash passing to the stack by about a third in comparison with dry-bottom operation.

5. The percentage of unburned combustible in the slag was small, but not negligible, in all cases.

6. Slagging-bottom operation increased the gas temperature below the boiler tubes by 300 to 400° F from what it was during drip-bottom operation.

7. Slag from the ash of the Pittsburgh coal could not be successfully tapped from the furnace of boiler 4 although the slag temperature attained was as high as that with the strip-mine coal, but this was attributed to an unfavorable location of the tap hole.

8. The slag from Pittsburgh coal was successfully tapped from boiler 5, owing not only to a more favorable location of the tap hole but also to a higher slag temperature as well as to a lower fluid temperature for the slag formed in this furnace.

9. The chemical composition of the slags formed from Pittsburgh coal in furnaces 4 and 5 was substantially the same and does not explain the differences in fluid temperature.

10. The slag from Georges Creek coal could not be tapped from furnace 4.

11. Experiments on the effect of adding fluxes to the Pittsburgh coal ash indicate that ferric oxide equivalent to 10 percent of the slag produced should flux the slag sufficiently to permit tapping.

The authors stated that caution should be exercised in generalizing from these observations because the furnaces were not originally designed for operation with a slagging bottom.

The studies described in this paper pro-

vided a basis for the development of a laboratory-scale investigation of the problem. The second paper of the series described some results obtained in small-scale and in large-scale laboratory tests in which a gas furnace having a slag hearth 2½ feet by 3 feet in area was used.

The small-scale tests were made in a platinum resistance furnace, the slags being contained in a platinum-rhodium crucible. A slag which had been tapped successfully at a known temperature in the experiments at the Toronto station was used as a standard of fluidity. Some of this slag was heated in the crucible to the temperature at which it had been successfully tapped, and its "feel" when stirred with a heavy platinum stirring rod was studied. The temperature at which a given slag exhibited the "standard feel" was designated as the "flow temperature" of the slag, and the experimental work consisted in determining the flow temperatures of a large number of coal-ash slags, both without and with additions of known amounts of various fluxes.

Nicholls and Reid recognized that it would be advantageous if the flow temperature could be predicted from one of the standard ash-fusion temperatures. The "fluid temperature" would appear to correspond most closely to the flow temperature, but neither it nor the "initial deformation temperature" correlated with the flow temperature as well as did the "softening temperature." From plots of flow temperature versus softening temperature they developed the empirical relationship

$$\text{Flow temperature (°F)} = (\text{Softening temperature} + 60) + (15 \times \text{Percent Fe}_2\text{O}_3)$$

but this equation did not hold closely enough to permit substitution of softening-temperature measurements for measurements of flow temperature.

It is quite impossible to summarize briefly and satisfactorily the results obtained with the various fluxes, which included borax, feldspar, fluorspar, saltcake, limestone, and iron oxide. In general it may be said that any of these materials, with the exception of feldspar, when added alone, lowered the flow temperature. Feldspar was tried with only two slags, and in both it raised the flow temperature. This result is to be anticipated since the ratio of silica plus alumina to the sum of the alkaline-earth and alkali oxides is higher in most feldspars than in most coal ashes.

The gas-furnace tests indicated that from the data obtained in the electric-furnace tests the amount of flux required to produce fluidity could be predicted, but the data were insufficient to permit an estimate of the time required for fluxing. The authors pointed out that certain questions need to be answered in connection with the latter problem. If it is assumed that sufficient flux to produce the required fluidity is spread uniformly on the surface of a bed of solidified slag, the upper surface of which is maintained at a definite temperature by combustion above it, there will exist a thermal gradient through the slag. The questions that must be answered are:

1. As reactions occur between the slag and the flux, what order of saturation of the flux will occur in the top layers of the slag; will it tend to become supersaturated?
2. At what rate will the flux progress through the bed? What will be its final distribution?
3. Will the upper and hotter layers tend to retain a higher percentage of flux and thus deprive the lower of the opportunity to become fluid, so that fluidity will decrease with distance below the surface?
4. Will a flux which is molten at the temperature of the surface have an advantage because of its molten condition?

Although the data were insufficient to answer these questions in detail it is inter-

esting to note that when limestone, dolomite, or fluorspar was applied to the top of the bed the surface layers ultimately showed a deficiency of the flux, and, since a composite sample of the slag showed that none of the added flux had been lost, it was apparent that, instead of remaining at the top of the bed, the flux tended to concentrate at the bottom.

Nicholls and Reid discussed the application of their results to the slagging-bottom furnace. They concluded that the commercially important fluxes are lime and iron oxide, and they described a method for computing the most economical proportions of these two fluxes to add to give any desired result.

The third paper of this series began with a consideration of the effect of the state of oxidation of the iron on the flow temperature of the slag. In this connection the later paper by Reid to which reference has already been made⁷⁶ should be examined. For convenience the idea of "ferric percentage" was introduced, namely, the percentage of the total iron in the slag (expressed as ferric oxide) that is actually in the ferric state. Mathematically this is given by the relationship:

$$\left. \begin{array}{l} \text{Ferric} \\ \text{percentage} \end{array} \right\} \frac{\text{Fe}_2\text{O}_3 \times 100}{\text{Fe}_2\text{O}_3 + 1.11\text{FeO} + 1.43\text{Fe}}$$

the quantities Fe_2O_3 , FeO , and Fe being determined analytically.

Nicholls and Reid summarized the effect of the ferric percentage on the flow temperature as follows:

1. With slags containing an equivalent Fe_2O_3 (that is, $\text{Fe}_2\text{O}_3 + 1.11 \text{ FeO} + 1.43 \text{ Fe}$) of 10 percent, the minimum flow temperature occurs at a ferric percentage of about 30.

2. As the iron content of the slag increases above 10 percent (equivalent) Fe_2O_3 , the ferric percentage for minimum flow temperature decreases and reaches 10, with slags contain-

ing, probably, about 20 percent equivalent Fe_2O_3 .

3. As the iron content of the slag increases beyond 20 percent, the decrease in flow temperature for a given decrease in ferric iron becomes greater.

4. With the same iron content and increasing lime (up to 16 percent), the influence of the state of the iron on the flow temperature becomes less when the iron content is low (10 percent) and is not affected if it is high (40 percent).

Because the flow temperature is a function not only of the three apparent variables ($\text{CaO} + \text{MgO}$), Fe_2O_3 , and ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) but also of the ferric percentage, it would require a series of diagrams at various ferric percentages to describe the composition-flow temperature relationship. However, Nicholls and Reid stated that analyses of slags from slag-tap furnaces showed that a ferric percentage of 10 was fairly representative. Figure 9 indicates the effect of variations in lime and iron content of the slags on their flow temperatures for ferric percentages of 10. These data apply particularly to slags having a silica to alumina ratio in the range of 1.7 to 2.0. A supplementary diagram permits flow temperatures calculated from Fig. 9 to be corrected for variations in ferric percentage from 10. Figure 9 is intended to be indicative of the nature of the relationship disclosed rather than for actual use. For a more precise diagram (isotherms every 25 degrees), as well as for the supplementary diagram, reference to the original paper should be made.

The fourth paper of this series described measurements of absolute viscosity made on coal-ash slags. The viscosity-temperature data obtained by Nicholls and Reid fell into two classes, depending on whether or not the slags devitrified easily at temperatures below the liquidus. The oscillating-bob type of viscometer was used, an

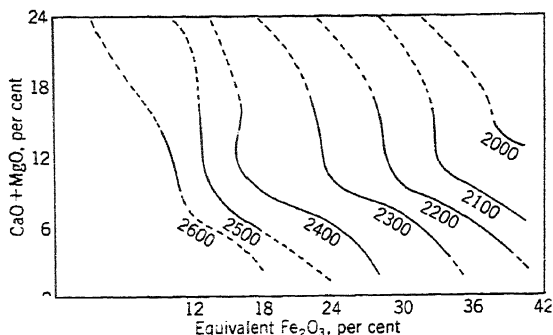


FIG. 9. Flow temperature of coal-ash slags. Data of Nicholls and Reid.²¹

instrument very sensitive to the presence of a solid phase. Consequently when measurements of viscosity were made at successively lower and lower temperatures very abrupt transitions from a finite to an apparently infinite viscosity occurred as soon as a solid phase began to separate in considerable amounts. Owing to the delay in crystallization and solution which characterizes melts high in silica, several heating and cooling cycles were necessary and the liquidus temperature for the slag was always somewhat in doubt. However, it evidently must lie between the two temperatures determined by successive heating and cooling cycles.

Figure 10 illustrates the above discussion and also shows the effect of the ferric percentage on the viscosity and liquidus temperature for a slag having a low equivalent ferric oxide content (13.3 percent in this particular slag). The authors summarized the effect of the ferric percentage for slags of low and moderate iron content as follows:

1. The shape of the viscosity curve is not changed by a decrease in ferric percentage, but the entire curve is raised about 20 percent (on the viscosity basis) above that for the melt in air.

2. The main effect of lowering the ferric

percentage is the decrease in the liquidus temperature.

3. There is little change in the liquidus temperature with change in ferric percentage for slags having an equivalent ferric oxide content of 12 percent and lower. As the iron content increases, the change in the liquidus also increases, but the exact amounts have not yet been determined for the entire range of coal ashes.

The paper did not report results of tests in nitrogen for slags of high iron content

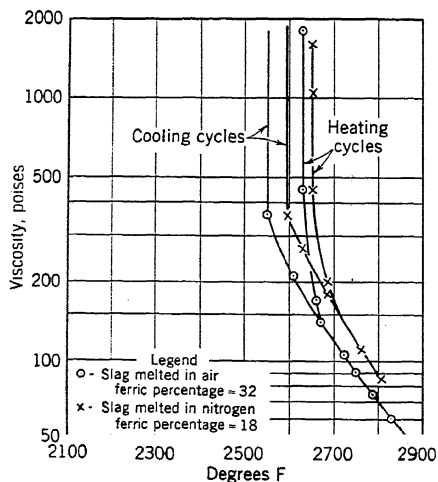


FIG. 10. Effect of ferric percentage on viscosity of a slag of low iron content. Data of Nicholls and Reid.²¹

because no container that will withstand the fluxing action of slags high in ferrous iron has been obtained. The authors predicted on the basis of their studies of flow temperature that a marked lowering of the

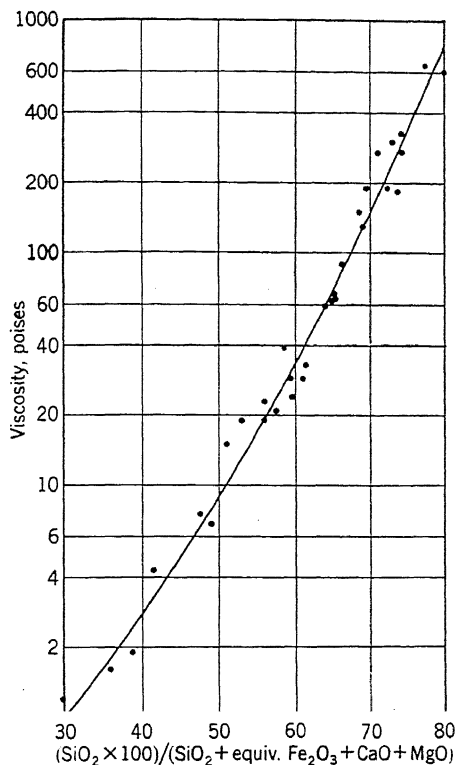


FIG. 11. Viscosity of coal-ash slag in air at 2,600° F. Data of Nicholls and Reid.⁸¹

liquidus temperature would accompany decreases in ferric percentage for slags high in iron.

A very important observation made by Nicholls and Reid was that silica is the most important single component determining the viscosity of coal-ash slags melted in air. Figure 11 shows the result of plotting the viscosity at 2,600° F for a considerable number of slags as a function of the silica content on the basis

$\text{SiO}_2 + \text{Equivalent Fe}_2\text{O}_3 \div \text{CaO}$

$\div \text{MgO} = 100$ percent

It is truly remarkable that these points determine so well defined a curve in view of the fact that the silica to alumina ratio of the slags ranged from 1 to 4 and the

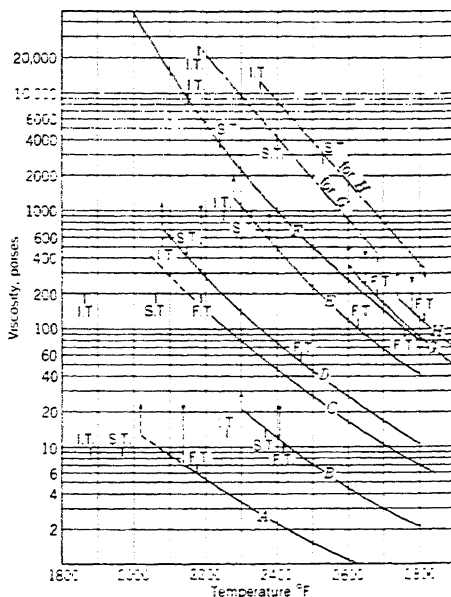


FIG. 12. Cone-fusion temperatures and viscosity curves for eight coal-ash slags. Data of Nicholls and Reid.⁸¹

ratio of ferric oxide to the sum of lime and magnesia ranged from 0.25 to 10.7.

It would be a decided advantage if a correlation between viscosity and fusibility of coal-ash slags could be found. Because fusibility measurements are made under reducing conditions a correlation, if any exists, should be found when viscosity measurements are made on slags of low ferric percentages. Figure 12 shows comparisons made by Nicholls and Reid between viscosity and initial deformation temperatures (I.T.), softening temperatures

(S.T.), and fluid temperatures (F.T.) for eight coal-ash slags of low ferric percentages. Examination of the figure shows the following:

1. The correspondence between fluid temperature and viscosity varies from a viscosity of 6 poises at the fluid temperature in ash A to a viscosity of about 190 poises at the fluid temperature for ash G.

2. The softening temperature for ash A is below the liquidus but that for ash B corresponds to a viscosity of about 15 poises. On the other hand the viscosity for ash F at the softening temperature is about 4,000 poises.

3. The initial deformation temperature is below the liquidus for most ashes but in ash D the initial deformation appears to occur fairly close to the liquidus and at a temperature corresponding to a viscosity of about 700 poises in contrast to ash F for which the initial deformation temperature corresponds to a viscosity of about 9,000 poises.

These observations indicate, as might be anticipated, that there is no relationship between the temperature at which an ash cone reaches a particular state of deformation and the viscosity of the corresponding slag. It will be recalled that the temperature intervals between the standard states of deformation of the cones were supposed to provide an index of the viscosity of the ash. As a test, Fig. 13 has been constructed. In the figure, temperature intervals between the softening and fluid temperatures and between the initial deformation and fluid temperatures have been plotted against the viscosities of the corresponding slags at 2,400° F. From the figure it is apparent immediately that these intervals are not even a qualitative guide to relative viscosities.

It should be noted that fusibility measurements used in Figs. 12 and 13 were made, not on the ashes, but on the slag remaining from the viscosity measurements. Analytical data for these slags are given

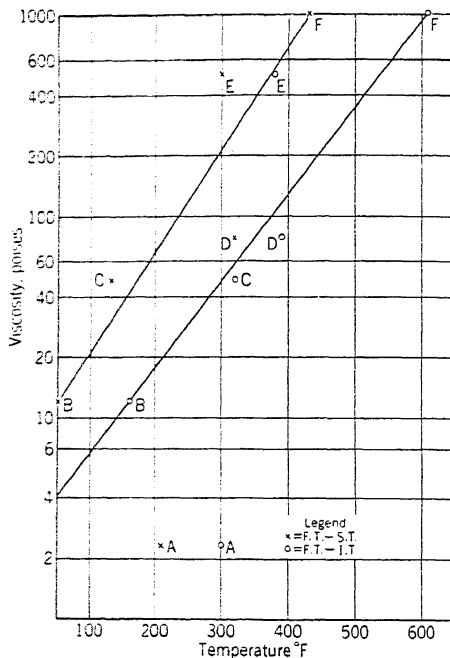


FIG. 13. Comparison of fusion intervals with slag viscosities. Data of Nicholls and Reid.⁸¹

in Table VIII, which shows the sum of the "fluxes" ferric oxide, lime, and magnesia for each slag; it will be observed that the viscosities shown in Fig. 12, generally speaking, increase as this sum decreases.

TABLE VIII

COMPOSITION OF SLAGS USED TO OBTAIN THE DATA OF FIG. 12

	A	B	C	D	E	F	G	H
SiO ₂	26.3	35.3	41.4	48.4	50.0	57.5	53.3	55.3
Al ₂ O ₃	11.6	16.6	22.3	19.2	26.7	19.1	28.3	31.1
Fe ₂ O ₃ (equiv.)	46.1	9.9	31.4	12.1	13.1	13.2	13.7	9.5
CaO + MgO	16.0	38.2	4.9	20.3	10.2	10.2	4.7	4.1
Fe ₂ O ₃ + CaO + MgO	62.1	48.1	36.3	32.4	23.3	23.4	18.4	13.6

Nicholls and Reid summarized their results by means of four trilinear plots, of which Fig. 14 is typical. The compositions are expressed on the basis

$\text{SiO}_2 + \text{Equivalent Fe}_2\text{O}_3 +$

$(\text{CaO} + \text{MgO}) = 100 \text{ percent}$

the alumina being eliminated. They stated that their limited data suggest that the viscosity of the slags is practically independent of the silica to alumina ratio over

roughly parallel to the coordinate lines showing the silica content of the slags, which is in accordance with the observations previously made that there is a fair correlation between increasing viscosity and increasing silica or between increasing viscosity and decreasing "flux" content. In

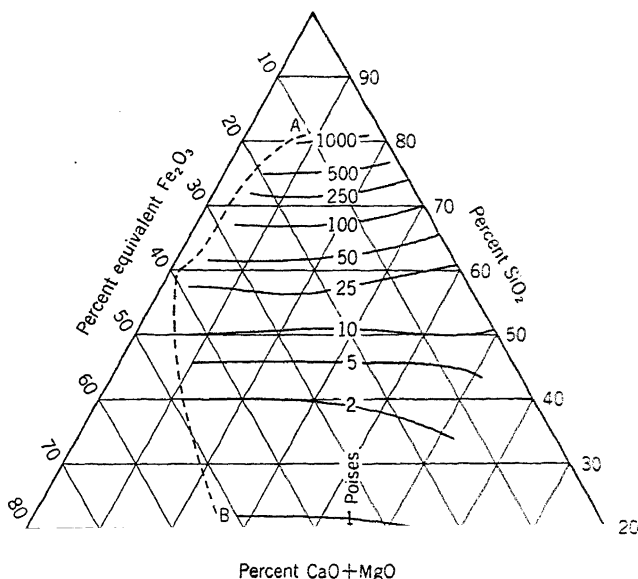


FIG. 14. Viscosity-composition relationship at 2,600° F for coal-ash slags melted in air. Data of Nicholls and Reid.²¹

the range from 1.5 to 3.0. Since most coal-ash compositions fall within this range the data can be used without correcting for variations in this ratio. They also stated that the slags contained not more than 2.5 percent alkali oxide. Data are not as yet available on slags of higher alkali oxide content.

In Fig. 14 the dotted line A-B is the liquidus boundary for the temperature of the figure, which is 2,600° F. Consequently compositions lying to the left of this line contain solid phase at equilibrium. It will be observed that the isoviscosity lines are

short, the sum of the "fluxes" is a fair index of slag viscosity.

Inspection of the figure shows that, in general, it is better to lower the viscosity of a slag by adding lime or a mixture of iron oxide and lime rather than by adding iron oxide alone, particularly if the lime content of the slag is low because the compositional area within which solid phase exists at equilibrium radiates out, so to speak, from the ferric oxide corner of the diagram. This becomes of more importance as the temperature is lowered and the liquidus area extends only to 30 per-

cent equivalent ferric oxide for slags containing 10 or more percent of lime plus magnesia. At this temperature slags containing less than 10 percent alkaline-earth oxide separate a solid phase regardless of the proportions of the other components. The authors⁵¹ emphasized that their plots were based on limited data, particularly as regards the relation between liquidus temperature and chemical composition.

slags. The practical advantage of this knowledge lies in the fact that if the viscosity of a slag at any temperature is known the viscosity at any other temperature can be computed approximately. This statement is, of course, subject to the limitation that, if the second temperature is below the liquidus, the slag must not devitrify.

The temperature coefficient of viscosity

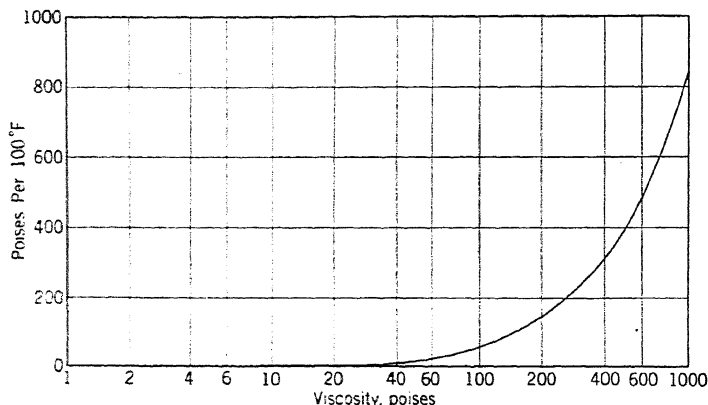


Fig. 15. Temperature coefficient of coal-ash slag viscosity. Data of Nicholls and Reid.⁸

Nicholls and Reid also showed that it is possible to construct a mean temperature-viscosity curve for coal-ash slags. If, starting with a set of temperature-viscosity curves such as those of Fig. 15, the curves are displaced parallel to the temperature axis until they coincide at some point with a curve, which for reference purposes is not displaced, they will be found to coincide, approximately, throughout their length; that is, the shapes of all the curves are substantially identical and, consequently, they can be fused into a single curve by translation parallel to the temperature axis. Theoretically, this signifies that the temperature coefficient of viscosity is substantially identical for all coal-ash

is not a constant but varies with the viscosity. Nicholls and Reid showed this variability as follows:

- At 1 poise, rate of change of
viscosity per 100° F = 0.28 poise
- At 10 poises, rate of change of
viscosity per 100° F = 4 poises
- At 100 poises, rate of change of
viscosity per 100° F = 58 poises
- At 1,000 poises, rate of change of
viscosity per 100° F = 850 poises

In Fig. 15 the writer has plotted these data on semilogarithmic coordinates, showing the temperature coefficient of viscosity as a function of viscosity.

Some of the slags studied in this investi-

gation were also used in the earlier studies of flow temperature. For some of these Nicholls and Reid made the comparison of flow temperature, viscosity at the flow temperature, and liquidus temperature shown in Table IX.

TABLE IX

COMPARISON OF FLOW TEMPERATURE, VISCOSITY, AND LIQUIDUS TEMPERATURE

Flow Temperature °F	Viscosity at Flow Temperature poises	Liquidus Temperature °F
2,550	9	2,550
2,350	16	2,300
2,580	20	2,550
2,685	78	2,280
2,730	80	2,700
2,390	80	2,150
2,570	85	2,500
2,560	90	2,200
2,500	120	2,400
+2,730	(100)	2,760

Regarding these data the authors made the following comments:

(a) Normally the flow temperature corresponds to a viscosity of about 80 poises.

(b) The flow temperature cannot be less than the liquidus temperature. Thus, if the viscosity at the liquidus is less than 80 poises, the viscosity at the flow temperature will also be below 80 poises. In Fig. 2 [see original paper], the viscosity at the flow temperature for melts in air was 9 poises. The observer could get very close values for flow temperature in a slag like this, because the melting range of slags high in iron is very short and the slag changes from plastic to liquid in the range of a few degrees.

(c) If the slag acted like a glass and had no liquidus point, or if the liquidus occurred at a viscosity much above 80 poises, the reaction of the observer was to decide on a value for the flow temperature when the slag had a viscosity greater than 80 poises. The flow temperature for a ferric percentage of 10 in Fig. 6 [see original paper] is an illustration.

In the investigation on flow temperatures, the aim was to fix its values so that different slags would tap with the same relative ease. This aim was fulfilled, even though the viscosities at the flow temperature are not all alike. Types of slags covered by item (b) will flow faster because of their low viscosities; to offset this advantage, they will solid-

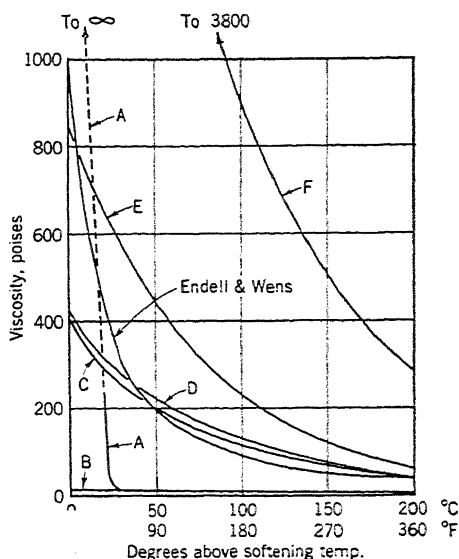


FIG. 16. Comparison of average viscosity curve of Endell and Wens⁷⁸ with data of Nicholls and Reid.⁸¹

ify with a small decrease in temperature and thus form "pipes" of slag, which clog the holes and decrease the flow. Slags covered by item (c) will flow more slowly because of higher viscosity but will be less hampered by rapid solidification and the clogging of the hole.

Figure 16 shows the average viscosity-temperature curve for coal-ash slags given by Endell and Wens.⁷⁸ It will be observed that these authors expressed viscosity as a function of the number of degrees above the ash-softening temperature. From what has been said above, it would not be expected that a single curve applicable to all coal-ash slags could be

obtained by this means. To demonstrate the inadequacy of such a curve the writer has converted the data of Nicholls and Reid given in Fig. 12 from Fahrenheit degrees to degrees above the softening temperature and plotted them in Fig. 16, using the same key letters to identify the slags. The inability of any single curve to describe the relationship for slags of widely varying compositions is quite apparent.

THE FLOW OF COAL-ASH SLAGS AT TEMPERATURES BELOW THE LIQUIDUS

It has already been pointed out that the term viscosity is quite equivocal when applied to slags at temperatures below the liquidus but above the lowest eutectic of the system. However, such slags may flow, and, when they do, the consequences of the flow may be of very considerable practical importance. Therefore, such flow must be considered, but, in referring to it, it will be well to designate it as plasticity or simply as flow. As distinguished from viscosity this plasticity has the characteristic that, however it is observed or estimated, its magnitude is not simply a function of composition and temperature. It is, therefore, not a fundamental property but a property which depends upon the physical history of the slag.

If a slag is heated to a temperature above the lowest eutectic of the system but below its liquidus temperature and maintained for a long time at this temperature a certain quantity of a solid phase will remain in equilibrium with the liquid phase, and, if the system is one for which the equilibrium diagram has been worked out, the proportions and compositions of the liquid and solid phases can be computed. If the slag is then heated to a temperature above the liquidus and again returned to the original temperature the same phases will ultimately be found to be present in

the original proportions. However, the equilibrium diagram gives no information on the size of the crystals of the solid phase or the extent to which they tend to interlock and retard movement. All that can be said with certainty is that, the longer the slag is maintained at the temperature in question, the larger the size of the individual crystals will become and, consequently, the greater their retarding effect on flow of the slag will become. Therefore, any method for estimating flow of the slag which aims at obtaining reproducible results must aim at controlling the crystal size of the solid phase. This means that the time during which the slag is maintained at the temperature of measurement must be carefully controlled, or else that the slag must be maintained at a temperature above the liquidus for a sufficient length of time to insure complete solution of the solid phase after which it must be cooled to the temperature of measurement in a definitely prescribed manner.

Whatever the mode of measurement, the observer will wish to be able to correlate the results with practical, full-scale experience. Therefore, it is probable that no single mode of preparing the slag for test and no single test method will suffice as an index of the various phenomena in which the operating man is interested.

If the problem in hand is that of tapping a slagging-bottom furnace the operator will wish to know how the slag flows after it has been maintained for many hours at some fairly constant temperature, say 2,600° F. For this purpose it would probably make little difference whether the slag were prepared for test by starting with the powdered ash, heating it to 2,600°, and maintaining it at this temperature for, say, 24 hours, or whether the preparation were carried out by heating the powdered ash to some temperature above the liquidus,

holding it there until complete solution had occurred and all gas bubbles had escaped, then dropping the temperature to 2,600° and maintaining it at this temperature for 24 hours.

On the other hand, in the problem of clinkering on grates the operator is concerned with what happens during a matter of minutes rather than a matter of hours. The mode of preparation, then, would naturally be determined by the nature of the particular problem. For example, the question whether or not the slag will flow sufficiently to form clinker that can readily be removed from a small, domestic, underfeed stoker operated at a moderate rating could probably be answered by starting in the conventional way with the powdered ash and observing its behavior on being heated at a moderate rate as in the A.S. T.M. method for fusibility determinations, or, if more detailed information on flow were desired, the method of Bunte and Baum could be applied. Galileeva⁸² has applied this method and believed that it can be used to predict the ability of a given coal to form slag. However, in the problem of the formation of troublesome sheet clinker in large furnaces operated at high ratings, the operator is concerned not with what happens when powdered ash is heated but with what happens to the slag as it is cooled, for in such equipment the bulk of the ash which remains in the fuel bed is liberated as molten slag from the incandescent surface of fuel particles. Under these conditions the questions which need to be answered include the following:

1. Will the molten slag flow out of the high-temperature combustion zone under the action of gravity, or will it be so viscous that it moves along with the fuel through the bed?

2. If the slag is transported, either by flowing under gravity or by the movement of the fuel, from a high-temperature combustion zone to a cooler zone, will it devitrify and cease to flow fairly quickly, or will it continue to flow at the lower temperature sufficiently to form a large aggregate?

In short, a preliminary approach to certain aspects of the clinkering problem can be made by answering the question: If a coal-ash slag is formed at a high temperature and is then subjected to a series of decreasing temperatures, will it flow a little or a great deal?

One way to answer this question would be to bring the powdered ash to a temperature high enough to represent the maximum temperature to which it would be subjected in the fuel bed and then to measure the change in the rate of shear under a constant force or the change in the force necessary to produce a constant rate of shear as the temperature was reduced according to some predetermined schedule by means of some device such as a cylinder rotating in the slag. Such a procedure, like any other that might be chosen, would be arbitrary, because the values obtained at various temperatures would be a function of the rate of cooling.

Another approach to the problem, which might be expected to throw light on the relationship between plasticity of the slag and certain types of clinker trouble, would be to determine the temperature at which a molten slag, formed at a high temperature, will stop flowing if it is cooled very rapidly. The significance of choosing a very rapid rate of cooling is that if a slag which is cooled rapidly devitrifies (crystallizes) sufficiently to stop flowing at a particular temperature, say 2,400° F, then this temperature at which flow ceased owing to crystallization is a minimum for this particular slag, because, if it devitrified suffi-

⁸² Galileeva, E. A., *Khim. Tverdogo Topliva*, **8**, 565-77 (1937).

ciently during rapid cooling to stop flowing at 2,400°, then, if it were cooled more slowly, crystallization sufficient in extent to prevent flow would occur at a higher temperature.

A number of practical difficulties are encountered in devising means for making a measurement of this sort. In measuring the rate of shear of a cylinder which is immersed in the slag and to which is applied a constant torque, the problem of erosion of container and cylinder by the slag is immediately faced, particularly with slags of high iron content under reducing conditions, which are of course of great interest. The same difficulty is encountered in measuring the rate of flow of the slag through an orifice of standard diameter under a standard force or the rate of flow of a standard amount of slag down an inclined plane. Another difficulty is the problem of cooling rapidly but at some definite rate, and at the same time making a practically continuous series of observations in order to determine the temperature at which, according to some arbitrary criterion, the slag has stopped flowing. In spite of all these difficulties, it appeared to the writer that the temperature at which a rapidly cooling slag would devitrify to a sufficient extent to cease flowing at an appreciable rate was of sufficient interest to attempt to estimate it.⁸²

In devising this method the difficulty of container erosion was eliminated by eliminating the container, and the difficulty of making observations while cooling at a definite rate was eliminated by substituting heating for cooling. This latter substitution sounds paradoxical, but it may be shown that by properly interpreting the results the desired information can be ob-

tained. The procedure may be summarized briefly as follows:

The ash is heated to a temperature above the liquidus and maintained at this temperature until evolution of gas has ceased. The molten slag so obtained is cast into billets $\frac{1}{2}$ inch in diameter and approximately $\frac{1}{2}$ inch high by pouring the slag into a steel ring resting on a steel plate at room temperature. As soon as a billet is cast it is dropped into a container of Sil-O-Cel to prevent the glass from shattering as the result of thermal shock. Examination of thin sections with the petrographic microscope has shown that billets made in this way are completely vitreous. To make a measurement, a billet is placed on a refractory base in a gas-fired, horizontal muffle-type furnace and heated at the rate of 15° F per minute until its height has diminished to 20 percent of its initial value. Observations of height are made at intervals by means of a cathetometer, and temperature measurements are made with an optical pyrometer.

It will be observed that this procedure yields data which exhibit the height of the billet as a function of temperature or, since the rate of heating is constant, as a function of time. The graphical expression of this functional relationship is conveniently designated as the "flow curve" of the billet, and the problem, once the flow curve has been obtained, is to extract from it the maximum possible information regarding the manner in which the slag would have behaved had it been cooled at some definite rate from the temperature at which it was cast into a billet instead of being cooled with great rapidity and then slowly reheated.

Figure 17, showing the flow curves for three coal-ash slags, will be used to illustrate the method of interpreting them so as to obtain the desired information. Con-

⁸² Barrett, E. P., and Taylor, J. A., *J. Am.* (1936).

sider first the flow curve for slag 1. The curve shows that the billet began to deform under its own weight at 1,700° F (point A_1), but its viscosity was so high that it did not begin to flow at all rapidly until 1,850° F was reached. At about 2,000° F the curve exhibits a point of inflection, the rate of deformation diminishing with increasing temperature, and at

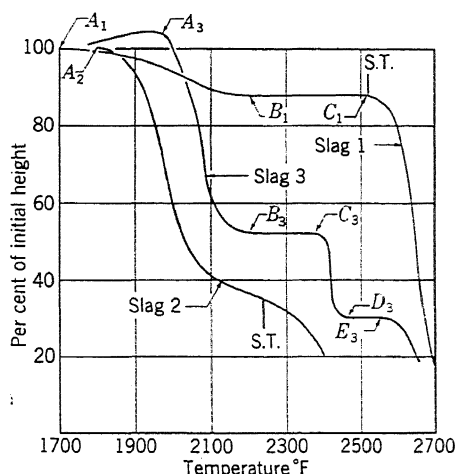


FIG. 17. Flow curves of three coal-ash slags.**

2,200° F (point B) flow ceased. At 2,510° F (point C) flow began again, and in the range 2,600 to 2,700° F the viscosity of the slag was only moderate as indicated by the rather steep slope of the curve. The significance of these phenomena is fairly obvious. In the range A_1 - B_1 the slag is very viscous and devitrification of the glass is occurring. By the time B_1 was reached crystallization had proceeded to the point where flow could no longer occur. The interval B_1 - C_1 is a solution range, and at C_1 sufficient solid phase has dissolved to permit deformation to resume.

What is the significance of these facts for the operating man who has to burn the coal in a piece of equipment operated at

high rating? In such a fuel bed there will exist a combustion zone in which the temperature is very high, 2,800 to 2,900° F. As the ash is liberated from the burning fuel it will form molten globules on the surface of the fuel particles, and as these globules grow larger, through coalescence as the fuel particle burns away, they will eventually reach a size such that they will flow downward under their own weight. This is evident from the slope of the curve in the range 2,600 to 2,700° F. As they flow downward out of the zone of intense combustion they will in general reach a region of lower temperature, say 2,200 to 2,300° F. Reference to the flow curve shows that if they remain in this region for any considerable length of time flow will cease owing to crystallization. This is demonstrated by the fact that devitrification was occurring at 2,000° F at a rate sufficient to retard the flow of the billet, and, if devitrification was going on fairly rapidly even at this low temperature when the slag was very viscous, it will certainly proceed at least as rapidly if the slag is maintained at a higher temperature but one which is materially below C_1 .

Suppose, on the other hand, that the coal being burned forms a slag represented by the flow curve for slag 2. This slag is much more fluid and, moreover, does not readily devitrify. That some crystallization does occur is evidenced by the diminished slope of the curve in the region 2,050 to 2,350° F, but at no time did this slag devitrify to an extent sufficient to prevent its deformation under so small a deforming force as its own weight. The curve shows that, to cause the flow of slag 2 to cease as the result of increasing viscosity, its temperature would have to be lowered to about 1,800° F. Such a reduction in temperature is too much to ask of large-scale equipment such as a large underfeed

stoker operated at high ratings. The temperature on the extension grate of such a stoker is probably considerably in excess of 1,800° F when the stoker is carrying a heavy overload. When slag 2 flowed down to a point near the tuyères it might be chilled to a temperature where flow would cease owing to increasing viscosity, but when it reached the extension grate it would begin to flow again and sheet clinker would form.

Under these conditions slag 1 would give relatively little trouble. Even if it flowed rather rapidly into a region where the temperature was considerably below 2,200° F, so that devitrification was retarded, it would quickly become very viscous and as it moved toward the extension grate it would continue to devitrify. The result would not be the formation of sheet clinker, and the size of the aggregates would not be likely to become so great as to give trouble in disposal through the dump grate.

The point to be emphasized is that both these coals form clinker, but the nature of the slag from only one of the coals is such that the clinker is likely to produce operating difficulties. That this conclusion is supported by practical operating experience is indicated by Ricketts' discussion of the problem,⁷² a portion of which was quoted on page 525. Slag 1 was formed from the ash of a typical West Virginia coal with an ash-softening temperature of 2,520° F. This coal has been burned on large underfeed stokers for the production of electric power without undue clinker trouble. Slag 2 was formed from the ash of a Pennsylvania coal with an ash-softening temperature of 2,240° F. This coal has given serious clinker trouble when burned on underfeed stokers at high ratings. It will be seen that these slags typify the distinction that Ricketts made in his discussion.

It is not suggested, of course, that the

mere geographical origin of the coals has any bearing on the behavior. The difference in behavior is to be ascribed to differences in ash composition, and by exercising some care in selection a Pennsylvania coal-ash slag could have been found to simulate the behavior of slag 1, and conversely; but before considering the influence of composition on the behavior of the slag a number of other points remain to be settled. Slags numbered 1 and 2 were selected simply because they threw light on Ricketts' observations. The softening temperatures of the ashes from which slags 1 and 2 were made are indicated by short vertical lines marked S.T. on Fig. 17. These softening temperatures bear no relation to the critical points on the flow curves which would give the useful information that the curves themselves provide. The inadequacy of the softening temperature in this respect will be further illustrated by data to be presented later.

The curve for slag 3 presents some interesting anomalies. The initial increase in height may be ascribed to high surface tension because the increase in height is brought about by the rounding of the flat bottom of the billet into a segment of a spheroid and is entirely analogous to the smoothing of a glass surface by "fire polishing." The occurrence of a second region of zero flow (D_3-E_3) may also be ascribed to surface forces because it was found that, wherever this phenomenon occurred, the slag did not wet the refractory base until the temperature corresponding to point E_3 had been reached. The failure of the slag to wet the base was indicated by the angle of contact of the billet with the base. Slags which flowed without wetting the base assumed a lenticular shape until point E was reached. At point E the angle of contact was 90°, and at temperatures above E the slag contacted the base at an angle greater

than 90° and flowed out over it horizontally instead of simply collapsing vertically and bulging so that its maximum horizontal cross-sectional area lay in a plane about halfway between the base and the top of the billet. This phenomenon might provide a means for estimating the temperature at which grate-bar erosion and slagging of refractories might be expected to become very serious.

In a type of flow curve exhibited by some slags the billet retains its initial form up to some temperature characteristic of its composition, after which it simply decreases in height in a uniform manner without any indication of devitrification or of flow arrested by surface forces. Such behavior indicates either that the slag never devitrifies or that it devitrifies so readily that the process is complete before the glass reaches a temperature at which it can flow under its own weight. For practical purposes it is of little importance which possibility accounts for the behavior since the practical question is whether or not the slag will stop flowing if its temperature is made lower than some value dependent on the construction and mode of operation of the particular equipment in which the coal is being burned. If the rate of flow is small, indicating a highly viscous slag, viscosity is the primary factor involved, whereas, if the flow is very rapid, devitrification is chiefly involved.

There is a pronounced similarity between this method of observation and that of Bunte and Baum.^{4, 6, 7} However, the behavior of a slag on cooling cannot be predicted with as much assurance from a measurement made on the pulverized ash as from a measurement on the slag itself. Some comparisons of the behavior of mixtures of the same composition in the form of billets and in the form of compressed briquets show identical behavior and others

wide variations. Agreement in behavior indicates that the particular compositions were ones which approached equilibrium rapidly from both the high- and low-temperature directions. A distinct advantage of the use of slag billets as test pieces is illustrated by Fig. 1S. Curve 1 is the flow curve of a billet. The curves marked 2 are

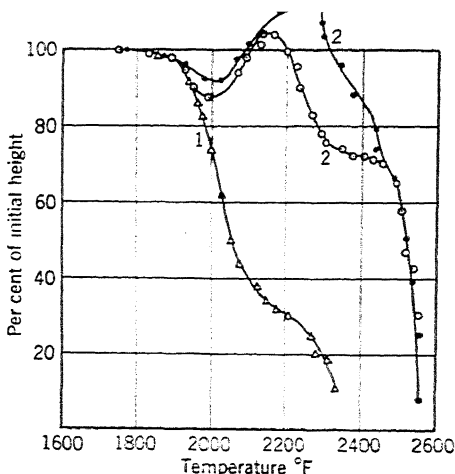


FIG. 1S. Comparison in behavior of billets and briquets.¹²

two measurements on briquets of the same composition as the billet. The behavior of the briquets was due to the evolution of gas trapped within the briquets. To some extent this could be overcome by applying a load to the cylinder of ash, as Bunte does, but, although the load may prevent an actual increase in height, it cannot prevent the gas trapped within the test piece from exerting a retarding action on the deformation until the liquid phase becomes low enough in viscosity to permit the gas to escape by bubbling through it. In any event it seems more reasonable, when one is concerned with the behavior of a slag, to make observations on the slag rather than on the ash from which the slag is derived.

A serious criticism of the procedure just described is that the state of oxidation of the iron is indeterminate. Although the failure to control the state of oxidation of the iron introduces some uncertainty, the flow curves indicate, in a qualitative way at least, the influence of composition on the behavior of slags. Figure 19 shows flow curves for mixtures of a particular kaolin

equivalent ferric oxide is increased the minimum temperature at which flow will occur is decreased markedly in the absence of lime and to a lesser extent with higher proportions of lime.

3. Increasing lime first raises and then lowers the viscosity.

4. Increasing iron increases the viscosity, very markedly when the lime is low

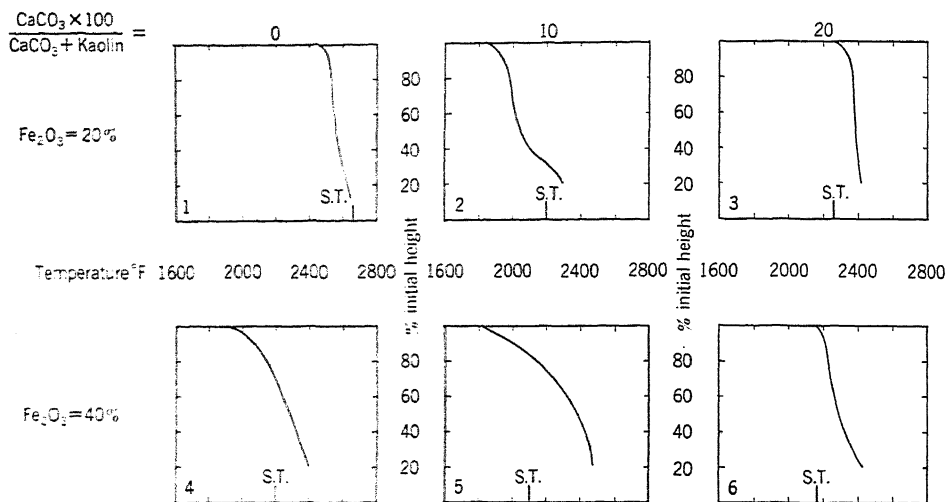


FIG. 19. Flow curves and softening temperatures of calcite-iron oxide-kaolin mixtures.

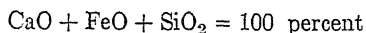
with various amounts of ferric oxide and calcite. Compositions 1, 2, and 3 in addition to containing calcite in the respective proportions of zero, 10, and 20 percent of the kaolin contain a constant amount, 20 percent, of equivalent ferric oxide. Compositions 4, 5, and 6 duplicate 1, 2, and 3 but contain 40 percent of equivalent ferric oxide. Inspection of the figure shows that:

1. If the proportion of equivalent ferric oxide is held constant and the proportion of lime to kaolin is increased, the minimum temperature at which flow will occur is first decreased and then increased.

2. If the proportion of lime to kaolin is kept constant while the proportion of

and to a lesser extent when the lime is increased.

The upper set of curves of Fig. 20 show, in somewhat greater detail, the effect of keeping the proportions of iron and silica constant and increasing the lime. These data are also for mixtures of kaolin, calcite, and iron oxide, but the compositions are expressed on the basis



The lower set of curves in this figure shows the effect of keeping the proportion $(\text{CaO} + \text{MgO}) : \text{FeO} : \text{SiO}_2$ constant and varying the quantity $(\text{MgO} \times 100) / (\text{MgO} + \text{CaO})$ between the limits of zero and 50.

The figures show that the composition-flow relationships are very complex as would be anticipated because not only viscosity but also devitrification is involved. The general inferences to be made appear to be:

increases the surface tension at low temperatures.

4. Figure 19 shows the absence of any relation between the softening temperature of the ash and the flow characteristics of the corresponding slag.

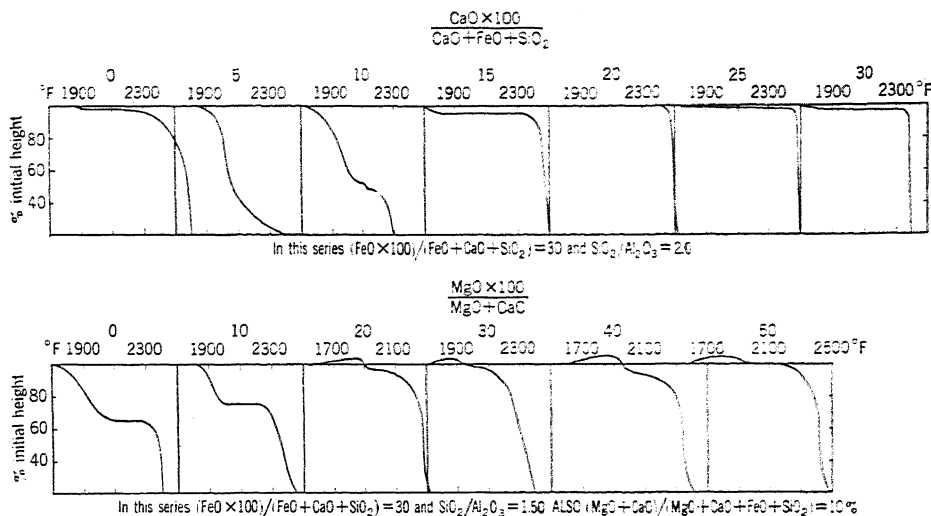


Fig. 20. Effect of alkaline-earth oxides on flow characteristics of synthetic slags.

1. If iron is kept constant, increasing lime first lowers and then raises the minimum temperature at which the slag will flow.

2. If iron is kept constant, increasing lime decreases the viscosity up to the highest percentage of lime used. This is in accordance with the observations of Herty, Hartgen, et al.,⁷⁷ who showed that viscosities in the lime-silica system decrease as the proportion of lime to silica approached the composition of calcium silicate which contains 48.5 percent lime. For the 30 percent lime mixture of Fig. 18 the quantity $(\text{CaO} \times 100)/(\text{CaO} + \text{SiO}_2) = 42.7$ percent.

3. Substituting magnesia for lime increases the ease of devitrification and in-

SUMMARY

1. The viscosity of coal-ash slags at temperatures above the liquidus and of slags that do not devitrify can be measured by the method of Nicholls and Reid,³¹ and, on the basis of their data, the composition of any slag can be so adjusted that it can be tapped at any temperature between 2,200 and 2,800° F.

2. Because of practical limitations the data of Nicholls and Reid have not yet been extended to include slags of high iron content under reducing conditions. Until a satisfactory container can be found for working with such slags under such conditions there appears to be no alternative to the procedure suggested herein as a means for studying their behavior.

3. Except in respect to slags which do not devitrify, the viscosity measurements of Nicholls and Reid cannot be extended to throw light on the problems of clinker formation. Until some more satisfactory method for estimating the temperature at which a cooling slag devitrifies sufficiently to prevent further flow has been devised, there appears to be no means for doing so other than studying the flow of cast billets in the manner described.

VARIOUS TYPES OF OPERATING TROUBLE ARISING FROM THE FUSION OF ASH

The operating difficulties arising from fusion and flow of ash cannot be discussed in the abstract but only by considering the consequences of burning coals of particular properties in particular ways in particular pieces of combustion equipment. Both the quantity of ash present and the distribution of the ash in the fuel are important factors. However, in order to simplify the discussion, it will be assumed, unless otherwise indicated, that the various ash components are distributed through the coal with sufficient uniformity so that, within limits at least, it can be supposed to behave in a manner related to its composition as determined by the usual ash analysis. This assumption can be justified to a considerable extent because coal which departs seriously from this condition is, in general, benefited by some sort of preparation process to correct its deficiencies if it is to be marketed for use in large-scale combustion equipment.

CLINKERING ON GRATES

In an overfeed fuel bed operating properly there are a series of layers, from top to bottom of the bed, which merge more or less gradually into one another. At the top is a layer of green coal which merges into a distillation zone where volatile matter is

being expelled. If a coking coal is being burned the distillation zone merges into a coking zone. Below the coking zone is a region of actively burning coke. If the draft is considerable, and particularly if the fuel bed is operating under forced draft, the temperature in this zone will be very high, frequently reaching 3,000 to 3,100° F, and the thermal gradients between it and the adjacent zones will be very great. Below this is a layer of ash or clinker or both.

In considering the conditions which may lead to the formation of large clinker, or to the adhesion of fused ash to the grate, or both, in such a fuel bed it is necessary to distinguish three conditions. If the temperature in the combustion zone is too low to cause appreciable fusion of the ash, clinkering, in the sense in which we are considering it, will not occur. As the fuel particles burn away, the ash particles are brought closer and closer together, and they eventually arrive at the grate as a more or less sintered mixture which gives no trouble. If the temperature in the combustion zone is high enough to fuse the ash but not high enough to reduce the slag viscosity to the point where individual globules of slag can migrate under the influence of gravity downward through the fuel bed, an accumulation of fused, but only slightly mobile, slag will occur as the fuel moves downward through the combustion zone, large aggregates will form, and there will be a large loss of combustible matter. If the ash content of the coal is high, the quantity of such aggregates may block the flow of air and combustion gases through the fuel bed. At best this may reduce the combustion rate that can be maintained, and at worst it may cause a rise in grate temperature to the point where the slag can wet the grate and adhere firmly to it. If the temperature in the combustion zone

is high enough not only to fuse the slag but also to lower its viscosity to the point where individual globules can migrate downward under their own weight, the situation becomes more complex and requires more minute analysis.

Other factors besides the physical properties of the ash and the combustion zone temperature affect the possibility of individual ash globules flowing through the fuel bed. The thickness of the bed, the size and size distribution of the fuel particles, and the quantity of ash are also operative, but we are here concerned only with the ability of fused slag to flow. If the conditions are such that the slag can flow, then, as individual fuel particles are gradually consumed by combustion, globules of fused slag will form on their external surfaces. As the combustion continues, the globules will grow larger owing to the liberation of more fused slag and will coalesce as the result both of their increasing size and of the diminution in surface of the fuel particles attendant upon combustion. When an individual slag globule becomes large enough it will break away from the burning fuel particle and flow rapidly downward. If it meets with no obstruction the ideal result is obtained; the globule falls through the grate bars and arrives in the ashpit where it almost instantaneously freezes into a small, glassy clinker.

If, on the other hand, the migrating slag globules meet with obstructions before passing through the grate bars, clinker trouble may or may not result, depending on the temperature to which they are exposed and on the properties of the slag. It was for the purpose of investigating the behavior of the slag under circumstances such as these that the method of testing described in the preceding section was devised. Suppose that the slag under consideration has the flow characteristics il-

lustrated by slag 1 in Fig. 17. Suppose further that the temperature in the combustion zone was 2,500 to 3,000° F, and that the temperature at the point above the grate at which the slag met with obstructions blocking its further progress was 2,300° F. From the flow curve for the slag it is apparent that, upon cooling to 2,300° F, rapid devitrification will occur and, unless the coal is very high in ash content so that a veritable rain of molten slag globules is arriving at this cooler region above the grate, no growth of large clinker can occur although, from the standpoint of ash fusion, all the ash that is not carried out of the fuel bed in the combustion gases is clinkering.

This state of affairs, or the one in which the slag flows all the way through to the ashpit, is eminently satisfactory. When the slag flows freely away from the surface of the burning fuel particles the loss of combustible in the ash is minimal, and, so long as the slag is one which devitrifies readily on moderate cooling, it is, in general, possible to construct and operate combustion equipment in such a way as to avoid unduly large clinker or the adhesion of slag to metal. In fact, most of the rules for design and operation of furnaces to avoid this type of clinker trouble are based on the principle of producing cool zones into which the molten slag will flow and solidify. So universally is this true that substantially all other rules for this purpose are based on the principle of avoiding heating a large proportion of the ash to or near its softening temperature at any one time.

Now suppose that the furnace conditions remain constant but that the slag, instead of having properties similar to those of slag 1 of Fig. 17, behaves like slag 2 in that figure. At the assumed combustion-zone temperature the slag will be very fluid and

3. Except in respect to slags which do not devitrify, the viscosity measurements of Nicholls and Reid cannot be extended to throw light on the problems of clinker formation. Until some more satisfactory method for estimating the temperature at which a cooling slag devitrifies sufficiently to prevent further flow has been devised, there appears to be no means for doing so other than studying the flow of cast billets in the manner described.

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is high enough not only to fuse the slag but also to lower its viscosity to the point where individual globules can migrate downward under their own weight, the situation becomes more complex and requires more minute analysis.

Other factors besides the physical properties of the ash and the combustion zone temperature affect the possibility of individual ash globules flowing through the fuel bed. The thickness of the bed, the size and size distribution of the fuel particles, and the quantity of ash are also operative, but we are here concerned only with the ability of fused slag to flow. If the conditions are such that the slag can flow, then, as individual fuel particles are gradually consumed by combustion, globules of fused slag will form on their external surfaces. As the combustion continues, the globules will grow larger owing to the liberation of more fused slag and will coalesce as the result both of their increasing size and of the diminution in surface of the fuel particles attendant upon combustion. When an individual slag globule becomes large enough it will break away from the burning fuel particle and flow rapidly downward. If it meets with no obstruction the ideal result is obtained; the globule falls through the grate bars and arrives in the ashpit where it almost instantaneously freezes into a small, glassy clinker.

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This state of affairs, or the one in which the slag flows all the way through to the ashpit, is eminently satisfactory. When the slag flows freely away from the surface of the burning fuel particles the loss of combustible in the ash is minimal, and, so long as the slag is one which devitrifies readily on moderate cooling, it is, in general, possible to construct and operate combustion equipment in such a way as to avoid unduly large clinker or the adhesion of slag to metal. In fact, most of the rules for design and operation of furnaces to avoid this type of clinker trouble are based on the principle of producing cool zones into which the molten slag will flow and solidify. So universally is this true that substantially all other rules for this purpose are based on the principle of avoiding heating a large proportion of the ash to or near its softening temperature at any one time.

Now suppose that the furnace conditions remain constant but that the slag, instead of having properties similar to those of slag 1 of Fig. 17, behaves like slag 2 in that figure. At the assumed combustion-zone temperature the slag will be very fluid and

will unquestionably flow readily. No harm will result if the fuel-bed conditions are such that the slag is unimpeded in its migration and flows through the grate into the ashpit. However, if the slag is retarded even briefly in a region below $2,400^{\circ}\text{F}$ it will rapidly become very viscous though not, unfortunately, sufficiently viscous to cease flowing altogether. Consequently a sticky, slowly flowing accumulation of slag will form in the vicinity of the grate, blocking off a large area of the fuel bed. If some of the slag reaches the grate it may adhere to the grate and ooze through between the bars with disastrous results. To burn successfully on grates at high ratings a coal the ash of which forms a slag of this sort, it is necessary so to design the equipment that the fluid slag is rapidly transported to a region where the temperature does not greatly exceed $1,800^{\circ}\text{F}$ and to clean the fire frequently enough to prevent accumulation of clinker to an extent sufficient to cause a rise in temperature significantly in excess of $1,800^{\circ}$.

Occasionally the composition of an ash yielding a slag with undesirable properties such as those of slag 2 of Fig. 17 is such that it is economically feasible to change its properties by the addition of inorganic material to the coal. Figure 21 illustrates an example. The ash yielded a slag which had the flow characteristics illustrated by the curve designated in the figure as "slag from untreated ash." The percentage composition of this ash was SiO_2 , 38.5; Al_2O_3 , 22.6; Fe_2O_3 , 18.9; CaO , 8.1; MgO , 1.1; $\text{K}_2\text{O} + \text{Na}_2\text{O}$, 1.9. Consideration of these data in the light of Fig. 19 indicated that the lime content of the ash was somewhat low in view of its iron oxide content. Consequently sufficient calcium carbonate was added to a portion of the ash to bring its lime content to about 13 percent. The ef-

fect of this addition of lime is shown in Fig. 21 in the curve marked "slag from treated ash." In view of the detailed discussion of flow curves and their significance the result requires no comment.

Clinker trouble of another type may occur in an overfeed fuel bed. A fuel bed operating with a combustion-zone temperature of $2,800$ to $3,000^{\circ}\text{F}$ on a coal the ash

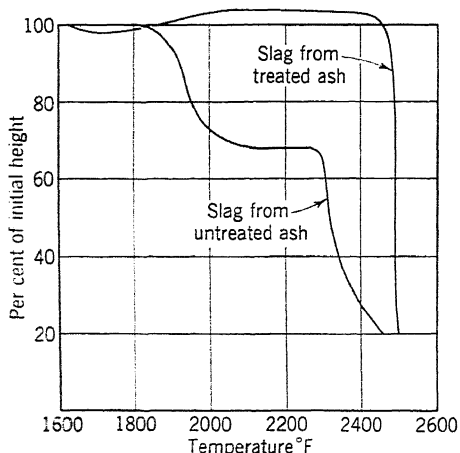


FIG. 21. Effect of addition of calcium carbonate on the flow characteristics of an ash.

of which yields, at these temperatures, a fluid slag that devitrifies readily at a temperature of $2,400^{\circ}\text{F}$ may operate indefinitely without giving trouble assuming that a mechanism exists for removing the discrete particles of small clinker produced under such conditions. However, if for some reason active operation is stopped and the fire is left under bank for many hours it frequently happens that a sheet of clinker forms at the bottom of the combustion zone half to three-quarters of an hour after normal operation is resumed. The condition under consideration should not be confused with the clinkering that may occur when a fuel bed that has been operating at a high rating is rapidly

banked. The sudden stoppage of the primary air under such circumstances permits excessively high temperatures and a strongly reducing environment in parts of the fuel bed and may result almost immediately in the formation of sheet clinker at the top of the ash zone. In the situation here being discussed the load is dropped reasonably slowly and the sheet clinker does not form until after normal operation has been resumed.

The mechanism by which the sheet clinker forms is quite obvious. While the fire is under bank slow combustion occurs with the liberation of ash at a comparatively low temperature and there is produced an accumulation of ash which is powdery or, at the most, sintered together. This, of itself, is a bad condition, but, aside from limiting the rating at which the equipment can be operated, it involves no serious consequences. Moreover, no serious operating difficulties would result if, when it was desired to resume normal operation, the temperature of the entire sintered mass could be raised suddenly to the temperature at which the slag would normally form in the combustion zone and at which it is fluid enough to flow readily under its own weight. Could this be done the entire mass would migrate downward, breaking up into discrete globules which, in colder regions below, would solidify. The release of this sudden shower of molten slag would, to some extent, interfere with normal operation for a short time, but in a little while these difficulties would disappear.

However, so ideal a state of affairs cannot be achieved. Of necessity the sintered mass will be heated up rather slowly, with the result that a temperature will be reached at which the slag begins a very slow viscous flow, the inevitable consequence of which is to seal off the fuel from

the air supply and a complete shutdown may result.

The means for combating this condition will depend on the size and construction of the unit. If physical conditions permit, the obvious procedure is to break up and disperse the sintered cake before the temperature is raised to a point where fusion begins. Frequently, however, the construction of the equipment does not permit such treatment, as, for example, in the Wood continuous gas producer, a type of unit in which this form of clinker trouble sometimes manifests itself. Probably the best solution is to wait until trouble begins to develop and then to feed steam into the primary air. This is a familiar procedure, but the mechanism by which it acts in circumstances such as these is frequently misinterpreted, the effect produced being ascribed to breaking of hard clinker by thermal shock. However, it is apparent that, when the trouble is due to the presence of a very viscous fluid, thermal shock must be discounted as a mechanism for relieving the condition. The fact is that the presence of even small amounts of moisture has a marked effect on the viscosity of slags in general. The phenomenon does not seem to have been quantitatively investigated, but it is known to be operative in the flow of certain volcanic magmas the composition of which is such that they would not, ordinarily, flow at the temperatures at which they are released but which do flow because of the lowering of their viscosity by the steam that is present. Consequently if steam can be brought into contact with a mass of liquid slag too viscous to flow under its own weight it is possible, frequently, to cause migration of the slag from a region where it causes operating difficulties to a region where it does not.

Thus far it has been assumed that we are dealing with what might be called the

"classical" overfeed fuel bed in which there are more or less definite strata from green fuel at the top to ash or clinker at the bottom. Frequently, however, when hand-fired fuel beds are operated at high ratings such a stratified condition does not exist owing to the tendency of the fireman to carry a thin fire and, particularly, if the coal is a heavily coking one, to work it frequently with a slice bar to keep it open and allow ready passage of air through the bed in order to maintain the desired rating. Under these conditions there is a tendency to bring aggregates of slag too viscous to flow under their own weight in contact with each other and to return them to the hottest region of the fuel bed with the result that every tendency for the formation of large clinker is fostered.

Frequently discussions of this source of clinker trouble stress the fact that such agitation returns the slag not only to a hotter region but also from an oxidizing environment near the grate to a more or less strongly reducing environment in the vicinity of incandescent coke, with resultant reduction of previously oxidized iron to the ferrous state and consequent lowering of the softening temperature. This explanation does not seem altogether satisfactory. If the ash which is returned to the high-temperature region has not already fused to form slag during its initial passage through the fuel bed it will not, in general, do so upon being returned to its former location. If it has been fused in its initial passage, a change in the oxidizing potential of the environment thereafter will not affect the state of oxidation of the iron except very slowly because the molten slag has a rather small specific surface and a gaseous reductant must penetrate into its interior by diffusion to reduce the iron there present. However, regardless of the mechanisms involved, it may be stated as

a general rule that any unnecessary agitation of a fuel bed is to be avoided as tending to aggravate clinker trouble.

Some of the more outstanding considerations involved in the formation of clinkers in the simplest type of overfeed fuel bed having been discussed, attention must be given to the more complex conditions existing in large furnaces operating in whole or in part on the underfeed principle. Nicholls⁸⁴ has shown that the time required for a piece of fuel to pass through the combustion zone in underfeed burning is four to five times as great as that required in an overfeed bed of the same depth and rate of burning. He showed also that the quantity of ash and clinker which accumulates in an underfeed fuel bed is several times as great as in an overfeed bed operating under comparable conditions. This demonstration depends upon the assumption that the slag does not flow but migrates with the fuel. This is a fair assumption but it cannot be considered to hold always, or even generally, after the combustible in the fuel particles has been reduced to 50 percent or less of its initial value. Nevertheless it is quite generally true that the large, multiple-retort stoker concentrates the ash in a way calculated to favor the growth of large clinker.

However, the formation of troublesome slag clinker in this type of underfeed stoker does not manifest itself within the fuel bed proper. The formation begins in the burning-out zone on the extension grate and builds back slowly toward the tuyères, blocking off the primary air supply from section after section until a shutdown is necessary. Ricketts⁷³ pointed out that not all coals yield slags which form troublesome clinker growth and that the tendency to form it is not directly related to the ash-

⁸⁴ Nicholls, P., *U. S. Bur. Mines, Bull.* **378** (1934), 76 pp.

softening temperature. Certain ashes, of relatively low softening temperature, tend, instead of forming sheets, to roll up in balls on the extension grate; unless they are too large to handle through the dump grate, they give no trouble.

In general the problem, from the operating point of view, is to achieve sufficient cooling of the extension grate region to prevent flow of the slag into sheet form. This problem, as has been indicated, is vastly complicated, and for the most part rendered impossible of solution, if the slag will not devitrify readily. Frequently when it is necessary to rely, not on devitrification, but upon increase in viscosity with falling temperature to stop flow, it is found that the temperature to which the extension grate region must be cooled to stop its flow is too low to be achieved while operating at efficiently high ratings.

By generalizing the remarks made regarding the particular problem of the formation of sheet clinker on the extension grate of multiple-retort underfeed stokers, it may be seen that the basis of all attempts to ameliorate the operating troubles attendant upon the formation of large clinkers in fuel beds is to cool those portions of the bed in which the ash is concentrated and that, the greater the concentration of the ash, i.e., the less the proportion of combustible associated with it, the greater must the cooling be. Regardless of the type of fuel bed the problem remains the same. The traveling-grate stoker, for example, causes the fuel, during the earlier stages of combustion, to burn on the underfeed principle; later the fuel passes through an intermediate or indeterminate type of burning; finally it burns out on the overfeed principle. Nicholls has very clearly illustrated this. Nevertheless the fundamental problem to be solved is still the same. As com-

busible burns away and aggregates of ash are brought closer and closer together, their temperature must be lowered to the point where flow is negligible.

Many of the authors who have discussed this problem stress the desirability of maintaining oxidizing conditions in regions where the concentration of ash is high with the object of keeping the iron in the ferric state. However, keeping the iron oxidized does not seem very feasible without introducing too great an excess of air. To raise the softening temperature of an ash containing considerable amounts of iron to a practically significant extent requires, in general, that the environment contain four or more times as much oxidizing gas as reducing gas. To achieve such a condition in particular regions of a large fuel bed presents a technical problem of such magnitude that satisfactory solution seems rather doubtful. On the other hand, cooling of particular parts of the fuel bed by the controlled distribution of air can be accomplished rather satisfactorily, and equipment so designed that the supply of air to different parts of the bed can be properly controlled not only is of material assistance in minimizing clinker trouble but also permits the maintenance of more satisfactory fuel-bed conditions in general, which, of itself, is a matter of importance in controlling clinker trouble. The control of clinker growth by controlled distribution of air was made the subject of patents by Evans⁸⁵ as long ago as 1913 and 1914, but since then the basic ideas have been elaborated in many different embodiments.

The matters considered in this section of the survey have been discussed by Bailey,⁸⁶

⁸⁵ Evans, O. B., U. S. Pat. 1,073,668 (1913). 1,085,806 (1914).

⁸⁶ Bailey, E. G., *Power*, 34, 802 (1911).

Bement,⁸⁷ Bro,⁸⁸ Calder,⁸⁹ Corcoran,⁹⁰ Glasgow,⁹¹ Marsh,⁹² and Rosin.⁹³ Rosin's paper contains a very detailed discussion of the technique of controlling the temperature in particular portions of the fuel bed by the controlled supply of air and by causing radiation to cooler surfaces to occur. The paper is well illustrated to show the application of the principles involved to particular types of combustion equipment. It merits careful reading by all students of clinkering problems.

In certain types of equipment the failure of the ash to clinker may present problems as serious as the formation of large clinker. The Wood continuous gas producer referred to above presents an example of this situation. In this gas producer the fuel rests on a bed of medium-sized clinker, and if the ash did not clinker operation of the producer would be impossible. Another illustration is the small domestic underfeed stoker which depends for ash disposal on the formation of clinker. The failure of some coals to form satisfactory clinker in such stokers has caused Sherman and Kaiser⁹⁴ to study the effect of addition agents to promote clinkering. That the production of clinker is not always a simple matter is demonstrated by the fact that Sherman and Kaiser concluded that borax and sodium silicate were the best materials to use for this purpose but that no addition agents changed the nature of the clinker very much and that their value would be mainly for unusual conditions.

⁸⁷ Bement, A., *ibid.*, 68, 683-4 (1928).

⁸⁸ Bro, L., *Chaleur et ind.*, 18, 105-14, 175-82, 215-24 (1937).

⁸⁹ Calder, G., *Steam Engr.*, 2, 249-50 (1933).

⁹⁰ Corcoran, J. L., *Power*, 75, 651-54 (1932).

⁹¹ Glasgow, A. G., Ger. Pat. 291,279 (1913).

⁹² Marsh, T. A., *Coal Age*, 17, 903 (1920).

⁹³ Rosin, P. O., *Braunkohle*, 30, 628-44 (1931).

⁹⁴ Sherman, R. A., and Kaiser, E. R., *Bituminous Coal Research, Inc., Information Bull.* 1 (1936), 10 pp.

SLAGGING OF REFRACTORIES AND GRATE-BAR EROSION

So far as slagging of refractories and grate-bar erosion are affected by the action of coal ash, the immediate cause of both sources of trouble is contact between the slag and a solid at temperatures high enough to permit the slag to wet the solid. It does not necessarily follow that, whenever a molten slag is in contact with one or more solid phases, solution of some of the components of the solid will occur. If the slag is saturated with respect to all the solid phases present no solution will occur; in general, however, this will not be the situation.

Probably the most thorough investigation of the slagging of refractories is that of Sherman,⁹⁵ who stated concisely the factors involved in the destruction of refractories by coal-ash slags in all types of furnaces:

1. Equilibrium conditions as given in phase-equilibrium diagrams for the components involved.

2. The rate of reaction, which is a function of:

- (a) Wetting of the refractory surface by the slag.
- (b) Penetration of the refractory by the slag.
- (c) Velocity of flow of the slag as determined by its viscosity.
- (d) Diffusion of dissolved refractory away from the interface and of furnace gas through the interface.

All the items under heading 2 are functions of the temperature. The wetting of the refractory surface is specifically a function of the temperature of the interface. No matter how hot the slag may be, so

⁹⁵ Sherman, R. A., *U. S. Bur. Mines, Bull.* 334 (1931), 144 pp.; *Fuel*, 10, 400-19, 445-58, 488-500, 531-38 (1931), 11, 28-35, 67-76 (1932).

long as heat transfer from the interface serves to keep it at a sufficiently low temperature, solution of components of the refractory in the slag will not occur even though at some time, owing perhaps to contact of a large mass of very hot slag, the interface was hot enough to permit wetting by, and consequent adhesion of, the slag. If, after adhesion has occurred, the interface can be kept cold enough to prevent solution, possibly by taking advantage of the thermal gradient through the layer of adhering slag, destruction of refractory will not occur. However, reaction can occur between solid phases at elevated temperatures even though the temperature is well below that of the lowest eutectic in the system.

These considerations apply with equal force to the problem of grate-bar erosion and the adhesion of slag to tuyères and other metal parts. These, in general, are more readily protected than refractories both because the solubility of metals in molten slag is much lower than that of refractories and because of their higher thermal conductivity.

Since iron and steel are subject to oxidation, a grate bar periodically exposed to a molten slag, which dissolves the oxide, may be slowly dissolved in the slag. In this connection, iron pyrites, because of its low viscosity and high specific gravity, flows readily and its insolubility in silicate melts permits it to behave as an individual component, particularly if it is present in the fuel in large lumps. Molten ferrous sulfide may dissolve as much as 15 percent of metallic iron owing to an eutectic at 1,832° F.⁹³

Regarding the utilization of the high thermal conductivity of metal parts, it has been demonstrated that, regardless of the temperature of the slag and of the environment, so long as the surface of a metal

plate could be kept below the temperature at which the angle of contact between a billet of the slag and the plate did not exceed 90°, firm adhesion did not occur.⁹⁶

Because the rate of solution of refractory components in a slag is a function of the area of refractory wetted by the slag, penetration of slag into pores of the refractory is a very serious matter. The total area of pores may readily be several hundred times as great as the apparent geometrical area through which the slag enters the pores. Consequently it has been found, as will appear later, that very high-grade refractories, as judged by composition and pyrometric-cone equivalent, sometimes display less resistance to slag attack than lower-grade refractories simply because insufficient glass phase is present to make the body dense and resistant to slag penetration.

Properly speaking, there are only two procedures for investigating experimentally the action of slags on refractories: the microscopic examination of the interface between refractory and slag after a definite heat treatment, and empirical methods. Ferguson⁹⁷ reviewed in detail the litera-

⁹⁶ Unpublished investigation by E. P. Barrett and J. A. Taylor. A steel plate was made part of the muffle floor of a gas-fired muffle furnace. Provision was made for air cooling of the plate and for measuring the temperature of its upper surface by means of a thermocouple inserted into a hole drilled from the bottom to the top of the plate and terminating just below its upper surface. A slag billet was placed on the plate and the furnace was heated, the temperature of the billet, the muffle walls, and the floor being explored with an optical pyrometer. It was found that, so long as the rate of air supply to the bottom of the plate was rapid enough to keep its surface temperature, as measured by the thermocouple, below that at which the angle of contact between slag and metal exceeded 90°, adhesion did not occur, regardless of furnace temperature or the degree of deformation of the billet. Results were independent of the chemical composition of the slag.

⁹⁷ Ferguson, R. F., *J. Am. Ceram. Soc.*, **11**, 90-8 (1928).

ture on laboratory methods for empirical study, and Simpson⁹⁸ has classified all laboratory methods. Much of the work done relates to other than coal-ash slags, and most of the laboratory-scale empirical methods yield results in forms which present difficult problems of interpretation if they are to be applied to coal-ash slags under furnace conditions. Klinefelter and Rexford⁹⁹ studied the phase equilibria involved and defined the "critical temperature" as that at which the principal solid phase disappeared from the slag and above which rapid solution of the refractory could be expected; Simpson¹⁰⁰ applied microscopic examination of the interface to a study of critical temperatures and slag attack for six coal-ash slags on eight refractories. Hursh and Grigsby¹⁰¹ and Hursh¹⁰² utilized a cylindrical revolving furnace, in which slag was fed into a gas flame that impinged upon the brick, in an empirical study, and, more recently, Fettke and Stewart¹⁰³ utilized a specially constructed powdered-fuel furnace for a very thorough study of slag erosion of different types of refractories by the ashes of several western Pennsylvania coals.

Simpson's procedure was to make a small crucible about $\frac{1}{2}$ inch in diameter and $\frac{3}{4}$ inch deep from a 1-inch cube of refractory cut from a standard 9-inch brick. The crucible was filled with the previously sintered coal ash and suspended in an elec-

trically heated furnace the temperature of which was automatically controlled within about 5° F. The crucibles were maintained at the desired temperature for 4 to 12 hours and then quenched by dropping them in running water. They were broken in half, and a thin section of the slag-refractory interface was prepared for study under the petrographic microscope.

Table X shows the composition and fusion characteristics of the coal ashes used by Simpson, and Table XI shows the maximum safe operating temperatures for the various ashes with the eight refractories tested.

Examination of Table XI shows that refractories fired to the higher temperatures resisted attack of the slags from the more refractory ashes (Detroit and Lowellville) better than the refractories fired to lower temperatures. For the moderately refractory ashes (Cahokia and Nanticoke), refractories fired to cone 12 were more resistant than those fired only to cone 6; but, for the lower-fusing ashes (Peoria and Chicago), little, if any, greater resistance was exhibited by the refractories fired at cones 12 and 14 than by those fired at cone 6.

Table XI also shows that the probability of improving a refractory by very fine grinding of the raw materials is only about one-half, improved resistance to the Peoria, Nanticoke, and Detroit ashes being effected by very fine grinding but no such improvement occurring for the Cahokia, Chicago, and Lowellville ashes.

It is interesting to note that a definite correlation exists between the method of manufacture of the refractories and their corrosion resistance, the stiff mud brick being superior to the hand-made and dry-press bricks. The two last types were identical except that the hand-made brick was slightly better as regarded the Peoria and the Detroit ashes.

⁹⁸ Simpson, H. E., *ibid.*, **15**, 536-44 (1932).

⁹⁹ Klinefelter, T. A., and Rexford, E. P., *Trans. Am. Soc. Mech. Engrs.*, **51**, 347-8 (1929), **53**, 301-5 (1931).

¹⁰⁰ Simpson, H. E., *J. Am. Ceram. Soc.*, **15**, 520-35 (1932).

¹⁰¹ Hursh, R. K., and Grigsby, C. E., *Univ. Illinois, Eng. Expt. Sta. Circ.* **17** (1928), 18 pp.

¹⁰² Hursh, R. K., *Trans. Am. Soc. Mech. Engrs.*, **51**, 339-45 (1929), **53**, 297-300 (1931).

¹⁰³ Fettke, C. R., and Stewart, W. E., *Mining and Met. Investigations, Carnegie Inst. Tech., Mining and Met. Advisory Boards, Coop. Bull.* **73** (1936), 84 pp.

TABLE X

COMPOSITION AND FUSION CHARACTERISTICS OF SIMPSON'S COAL ASHES¹⁰⁰

Percentage Composition of Coal Ash						
Coal Power Plant	Illinois Peoria	Illinois Chicago	Illinois Cahokia	Pa. Anthracite Nanticoke	W. Va. Pa. Detroit	Bituminous Lowellville
SiO ₂	41.9	42.5	52.6	56.8	49.9	56.9
Al ₂ O ₃	14.7	16.3	24.3	24.0	29.3	28.4
Fe ₂ O ₃	20.3	25.6	13.7	10.9	11.0	10.3
CaO	12.8	6.6	4.2	4.3	4.4	1.3
MgO	0.8	1.1	1.1	1.0	0.9	0.8
SO ₃	7.5	4.6	1.7	0.2	1.5	0.3
P ₂ O ₅	0.4	0.3	0.1	0.1	0.3	0.2
Alkalies (by difference)	1.6	3.0	2.3	2.7	2.7	1.8
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
SiO ₂ /Al ₂ O ₃ ratio	100.0	100.0	100.0	100.0	100.0	100.0
	2.85	2.61	2.16	2.37	1.70	2.01

Cone-Fusion Tests of Coal Ash

Critical Points, °F				Fusion Range, °F		
Coal Ash	Initial Deforma- tion	Softening Tempera- ture	Fluid Tempera- ture	Start to Down Point or "Softening Interval"	Down Point to Fluid or "Flowing Interval"	Start to Fluid or "Total Fusion Interval"
Peoria	970	2,020	2,360	50	340	390
Chicago	990	2,060	2,400	70	340	410
Cahokia	100	2,160	500	60	340	400
Nanticoke	250	2,290	560	40	270	310
Detroit	240	2,350	620	110	270	380
Lowellville	2,360	2,470	2,750	110	280	390

The quantities in parentheses in Table XI are not part of the original table but were inserted by the writer. The quantities under the names of the ashes are the A.S.T.M. fluid temperatures of the corresponding ashes as shown in Table X. Those under the maximum safe operating temperatures are the number of Fahrenheit degrees by which the fluid temperature of the ash fails to fall within the critical range for the ash-refractory combinations as found by Simpson. Inclusion of these quantities shows directly a correlation between fluid temperature of the ash and the critical range which Simpson has not explicitly mentioned.

Examination of these quantities shows a definite trend. The fluid temperatures of the least refractory ashes (Peoria and Chicago) were generally lower than the lower limit of the critical range. Generally, where this was not so, the fluid temperatures lay at the lower limit, and the only exception fell within the range. The fluid temperatures of the ashes of intermediate refractoriness (Cahokia and Nanticoke) were generally within the critical range or where this was not so the fluid temperature exceeded the upper limit of the critical range. The one exception to this generalization was out of line with the general trend. The fluid temperatures of the most refrac-

TABLE XI

MAXIMUM SAFE OPERATING TEMPERATURES OF ASH AND REFRACTORY COMBINATIONS ($^{\circ}\text{F}$)¹⁰⁰

Refractory	Ash					
	Peoria (2,360)	Chicago (2,400)	Cahokia (2,500)	Nanticoke (2,560)	Detroit (2,620)	Lowellville (2,750)
ST 1						
Dist. 1						
Dry press	2,300-2,375	2,400-2,600	2,400-2,450	2,400-2,550	2,500-2,600	2,600-2,700
Fine grind			(+50)	(+10)	(+20)	(+50)
Cone 6						
ST 2						
Dist. 1						
Dry press	2,400-2,450	2,500-2,600	2,400-2,500	2,500-2,600	2,400-2,600	2,600-2,700
Fine grind	(-40)	(-100)			(+20)	(+50)
Cone 12						
ST 3						
Dist. 1						
Dry press	2,450-2,500	2,500-2,600	2,500-2,600	2,500-2,600	2,500-2,600	2,600-2,700
Fine grind	(-90)	(-100)			(+20)	(+50)
Cone 14						
ST 4						
Dist. 1						
Dry press	2,500-2,550	2,500-2,600	2,400-2,500	2,500-2,700	2,600-2,700	2,600-2,700
Very fine grind	(-140)	(-100)				(+50)
Cone 12						
ST 5						
Dist. 1						
Stiff mud	2,400-2,600	2,500-2,700	2,500-2,600	2,600-2,700	2,600-2,750	2,700-2,800
Fine grind	(-40)	(-100)		(-40)		
Cone 12						
ST 6						
Dist. 1						
Hand made	2,400-2,500	2,500-2,600	2,400-2,500	2,500-2,600	2,500-2,600	2,600-2,700
Fine grind	(-40)	(-100)			(+20)	(+50)
Cone 12						
ST 7						
Dist. 2						
Dry press	2,400-2,500	2,400-2,500	2,500-2,600	2,450-2,550	2,500-2,600	2,550-2,650
Fine grind	(-40)			(+10)	(+20)	(+100)
Cone 12						
ST 8						
Dist. 3						
Dry press	2,400-2,500	2,400-2,600	2,500-2,600	2,400-2,600	2,500-2,600	2,600-2,700
Fine grind	(-40)				(+20)	(+50)
Cone 12						

tory ashes (Detroit and Lowellville) were generally higher than the upper limit of the critical range, and when this was not true the fluid temperatures fell within the critical range.

It would seem that these observations

might be made the basis of a set of empirical rules for preventing damage to fire-clay refractories by coal-ash slags somewhat as follows:

1. If the fluid temperature of the ash is below $2,400^{\circ}\text{F}$ the temperature of the

slag-refractory interface should not be allowed to exceed a temperature 150 to 200 Fahrenheit degrees below the fluid temperature of the ash.

2. If the fluid temperature of the ash lies between 2,400 and 2,600° F the temperature of the slag-refractory interface should not be allowed to exceed a temperature 50 to 100 degrees below the fluid temperature of the ash.

3. If the fluid temperature of the ash is higher than 2,600° F the temperature of the slag-refractory interface should not be allowed to exceed a temperature zero to 50 degrees below the fluid temperature of the ash.

It is interesting that the slag-refractory interface of the least refractory ashes may be heated 40 to 140 degrees above the fluid temperature of the ash before rapid solution of refractory begins whereas the fluid temperature of the most refractory ashes may lie as much as 100 degrees above the upper limit of the critical range. However, the circumstances appear merely to reflect the familiar rapid increase in reaction velocity with rising temperature.

As previously stated, Hursh¹⁰² and Hursh and Grigsby¹⁰¹ used a rotating furnace. They found (1) that the relative action of different slags at 2,900° F was a function of the composition and fusibility of the ash; (2) that the rate of erosion increased with decreasing furnace temperature and with increasing furnace temperature; (3) that the effect of changes in the reducing potential of the environment was small; (4) that the large thermal gradient resulting from the use of refractories of high thermal conductivity diminished slag attack on such refractories; (5) that materials of low refractoriness or those fired at high temperatures showed reduced resistance to slag attack due to diffusion of slag into the glass phase of the refractory;

(6) that the composition and structure of the refractory should be such that it will develop an impervious layer with a minimum of glass at the slag-refractory interface, for, if some vitrification of the refractory does not occur at furnace temperatures, slag penetration results; (7) that high-alumina bricks are superior to fireclay when the slag is low in lime and high in iron, but when lime is high, fireclay is superior; and (8) that the order of resistance of fireclay refractories to slag attack is the same as that of their densities. They concluded that the rotating-furnace test method gave results comparable to those of boiler furnaces operated at the same temperature.

Instead of the rotating furnace of Hursh and Grigsby, Fettke and Stewart¹⁰³ used a cylindrical furnace made of arch brick and fitted with a specially constructed rotating burner which gave a flame shaped like the frustum of a hollow cone. A "Coal Jet" pulverized-coal feeder supplied fuel and primary air to the burner. Secondary air was furnished by a "Premix" blower. In each test sufficient coal to give 500 pounds of ash was burned, after which the temperature of the test was maintained for 4 hours by using gas in the Premix in order to drain off excess slag from the surface of the refractories. The furnace was then allowed to cool at a rate of 50 to 100° F per hour to 1,000° F, after which the burner was shut off and the furnace allowed to cool to room temperature.

The erosion loss was measured in two ways. The volume before and after testing was measured by means of a mercury balance, and the volume before and after testing was calculated from direct linear and angle measurements made with a scale graduated to hundredths of an inch and a contact goniometer.

Fettke and Stewart found that the re-

sistance of different types of refractories varied with composition, the different types increasing in resistance in the order: forsterite, silica, chromite, magnesite, high-heat-duty flint fireclay, super fireclay, intermediate mullite, high alumina (diaspore type), high alumina (electrically fused type), high mullite (bonded type), cast mullite, silicon carbide. The erosion of refractories by coal ash was shown to be dependent on ash composition and related to ash-softening temperature to the extent that no erosion occurred until the temperature of the refractory face exceeded the softening temperature. They confirmed the previous observations of a "critical range" and noted that it corresponded to the temperature at which interfacial tension became low enough for wetting to occur. At this stage the solid phases of the coal ash had dissolved in the liquid phase, leaving it unsaturated with respect to some of the components of the refractory. The rate of slag attack was found to be proportional to increases in temperature above the critical temperature, and, in aluminosilicate refractories, a change in the temperature coefficient of erosion was noted above 2,700° F. This was ascribed to a lowering of the 2,813° F solidus line of the alumina-silica equilibrium diagram to about 2,710° F by the iron in the slag, in consequence of which a change to mullite and liquid occurs above this temperature with a weakening of structure and solution of the mullite by the liquid.

The tests indicated that the mechanism of slag attack on refractories is, primarily, one of solution. The rate of diffusion did not appear to be a governing factor. However, diffusion should be considered if no flame impingement occurs and the slag is relatively stagnant. Iron oxide was shown to be responsible for more damage than any other single component of the ash.

More recently Fehling¹⁰⁴ has made a very elaborate mathematical analysis of the problem, resulting in the relationship

$$\epsilon = \text{Const.} \frac{S_T}{\eta^{5/6}} \left(\frac{T}{r} \right)^{3/2} \left(\frac{\sin \alpha}{l} \right)^{3/2} \left(\phi \frac{BA}{fH_i \gamma} \right)^{1/2} \quad (1)$$

in which ϵ = the rate of erosion perpendicular to the surface of the wall in centimeters per second.

S_T = the solubility of the refractory in the slag in grams per gram.

η = the viscosity of the slag in poises.

T = the absolute temperature.

r = the molecular radius.

α = the angle of inclination of the wall.

l = the length of the wall in the direction of flow of the slag in centimeters.

ϕ = the fraction of the total ash or slag released which impinges upon the wall.

B = the loading of the combustion chamber or furnace in calories per cubic centimeter.

A = the ash content of the coal in grams per gram.

f = the ratio of furnace area to furnace volume in square centimeters per cubic centimeter.

H_i = the net calorific value of the coal in calories per gram.

γ = the specific gravity of the slag in grams per cubic centimeter.

To test his equation Fehling utilized the data of Fette and Stewart¹⁰³ and, since their furnace was always the same, was able to simplify equation 1 to the form

$$\epsilon = \text{Const.} \frac{S_T}{\eta^{5/6}} T^{3/2} (\phi BA)^{1/2} \quad (2)$$

¹⁰⁴ Fehling, H. R., *J. Inst. Fuel*, **11**, 451-58 (1938).

Figure 22 compares the measured erosion rates with rates computed from equation 2. Because of variability in the refractory itself, Fettke and Stewart found it impossible to reduce the variability in check runs to less than ± 50 percent. Therefore dotted lines showing a 50 percent spread are included in the figure. It will be noted that the points fall, substantially, within the triangle defined by these lines, and it may be said, therefore, that Fehling's equation describes the results within the limits of experimental error. The failure of the average line to pass through the origin is explained by Fehling by pointing out that when the furnace temperature is less than 50 Centigrade degrees above the ash-softening temperature, which it generally is for small values of erosion rate, the surface tension of the slag is too high to permit it to form a coherent film.

In view of all the difficulties in the way of developing a satisfactory equation the data support the theory remarkably well. The most serious defect in the assumptions is the failure to take into account the porosity of the refractory, but there seems to be no way to take account of it analytically. It appears that by means of Fehling's method an estimate of the relative slagging action of various ashes may be derived without recourse to expensive experimental investigations.

It is apparent that, although Fehling's equation involves twelve variables, two are of outstanding importance, solubility and viscosity. Both are functions of temperature, which brings us back to the basic problem of controlling temperature in particular regions of the furnace, in this instance the interface between slag and refractory.

It seems hardly necessary to discuss the implications of the information summarized in this section of the survey for practical

operation. The problem is clearly one of controlling the temperature at an interface. Controlled distribution of air, the use of which in the prevention of clinker growth was stressed in the preceding section, is one general means of limiting erosion. This means is utilized in some underfeed stokers,

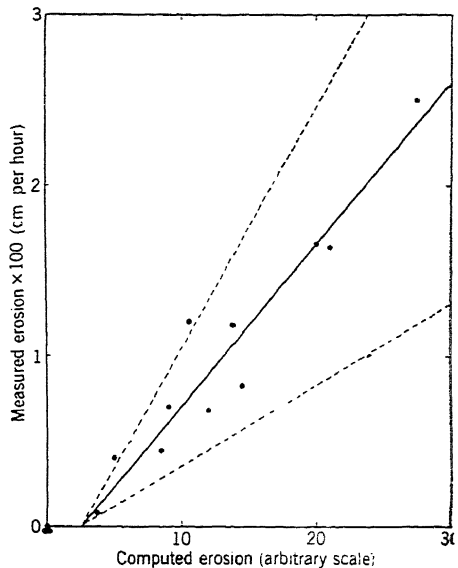


FIG. 22. Comparison of measured and computed erosions.¹⁰⁴

for example, by having ports in the side-wall refractories, in the vicinity of the hottest regions, through which air is blown to function both for cooling the refractory surface and as secondary air. Water-cooled refractories or water-cooled metal walls offer alternative solutions. The particular means chosen will depend on mechanical rather than physicochemical considerations.

SLAGGING OF HEATING SURFACES BY FLY ASH

The theoretical considerations involved in the problem of tube slagging are substantially the same as those determining

adhesion to grate bars and tuyères, which were considered in the preceding section. However, because the physical properties of the slag are a function of its chemical composition and because, in the fly ash, segregation of ash components occurs to a very marked extent, the slagging of tubes and other heating surfaces is not related to the average composition of the ash in the same way as is the slagging of grates and tuyères.

So long as the ash-forming minerals remain in the fuel bed the composition of the slag formed bears some relationship to the average composition of the ash, provided, of course, that the coal has received a reasonable amount of preparation calculated to eliminate large mineral aggregates such as pieces of slate, shale, and iron pyrites. Consequently the molten slag produced and remaining in the fuel bed has properties related, within limits, to the average composition of the ash. The ash which is carried out of the fuel bed, however, does not have the same composition as that of the average ash, and, even if it did, it is not to be supposed that its behavior on reaching a heating surface would be that predicted from its average composition.

If a mechanical mixture were prepared by fine grinding and intimate mixing of the slag components, the first liquid phase that would appear on heating the mixture would have the composition and properties of the lowest-melting eutectic in the system. If, as fast as liquid of eutectic composition formed, it was removed by mechanical means from the system, it would yield a slag quite different in properties from those which would be predicted from the average composition of the mixture of solid phases from which it formed. In a fuel bed, of course, such an ideal condition of fine subdivision and intimate mixture does not exist. Consequently there will be a

tendency for low-melting components to fuse independently, and, if they do not form solutions with other components before being caught by the stream of combustion gases, they may be carried out of the fuel bed as individual droplets of fairly pure chemical compounds. Likewise, higher-fusing components which happen to be liberated from the burning fuel out of contact with lower-melting components in which they might dissolve may be carried out of the fuel bed as fairly pure chemical entities without being fused.

The net effect of all these mechanisms is to bombard the tubes with a mixture of molten slag and unfused or only sintered ash in which the liquid phase, in general, will be much lower melting than would be expected from the average composition of the ash. However, so long as the interfacial temperature between the heating surface and the molten droplets striking it does not lower the interfacial tension to the point where wetting will occur, no adhesion can result; but in a large boiler furnace, where the tubes may be subjected to a veritable rain of low-fusing slag droplets, it is not surprising that adhesion occurs in spite of the cooling of the interface by the high thermal conductivity of the metal. It is only necessary for an infinitesimally thin layer of the tube to reach the temperature of wetting to permit adhesion of slag, and, once a layer of slag has formed, growth in thickness of the layer is inevitable. The slag has a low thermal conductivity, and successive droplets progressively raise the temperature of the surface exposed to the combustion gases. Once the layer is thick enough to remain sticky, even the unfused material striking it can adhere, and growth proceeds rapidly.

Because iron pyrites is the source of the lowest-melting compound in ash-forming minerals in most coals and because fayalite

(ferrous orthosilicate) forms a low-melting eutectic with silica it would be anticipated that the first layer of slag laid down on a heating surface would be a mixture of ferrous sulfide and fayalite. Oxidation and solution of other ash components would result in the formation of a layer of glassy slag, and, while the slag was sticky, considerable quantities of unfused or partly fused material would be trapped and held.

Experimental verification of the foregoing considerations has been obtained by Moody and Langan.⁷² They took samples of slag from the water wall fin tubes of a Springfield cross-drum boiler under which had been burning a Pennsylvania coal the ash of which had a softening temperature of about 2,700° F. The inner portion of the slag adjacent to the tube was not completely fused; it consisted of a honey-combed, sintered mass with spots of what appeared to them to be pure ferric oxide. The center portion appeared to be black glassy slag which had been completely fused, and the outer layer was an unfused conglomerate of ash adhering to the glassy interior.

Moody and Langan analyzed representative samples of the three layers of the slag and measured initial deformation and softening temperatures with the results shown in Table XII.

That such large differences between the softening temperature of the original ash and that of the tube slag are not exceptional is demonstrated by the data of Jacobus and Bailey,¹⁰⁵ who showed that, in general, the softening temperature of flue dust is higher and that of tube slag markedly lower than that of the original ash.

Moody and Langan pointed out that the composition and properties of the ash and slag carried out of the fuel bed depend

TABLE XII

ANALYSES OF SLAG SAMPLES REMOVED FROM
SPRINGFIELD BOILER USING A PENNSYLVANIA
COAL ⁷²

Item	Next to Tube percent	Fused Center percent	Outer Section percent
SiO ₂	41.7	45.3	51.5
Al ₂ O ₃	30.9	32.5	29.0
Fe ₂ O ₃	19.5	15.3	12.9
CaO	8.7	7.7	4.0
MgO	Trace	Trace	Trace
Total	100.8	100.8	97.4
Initial deformation temperature (°F)	2,165	2,200	2,320
Softening temperature (°F)	2,200	2,230	2,395

upon the relative amounts of inherent and extraneous ash in the original coal and the distribution of the fluxes, lime and iron, between the inherent and extraneous ash. They believed that if the larger proportion of these fluxes are concentrated in the extraneous ash then, since the extraneous ash is in a coarse state of aggregation compared to the inherent ash, the fluxes will tend to remain in the fuel bed and the more finely divided refractory ash will tend to be carried out, with the result that the ash remaining in the fuel bed will be more fusible than the average ash of the coal.

They described two methods of fractionating the ash of a coal to estimate its behavior in this respect: one a liquid classification method, the other a method of screening the ash. Both methods divided the ash into size ranges, and softening temperatures of each size range were determined.¹⁰⁶ If the coarse sizes showed lower softening temperatures, the fusibility of the ash remaining in the fuel bed would be ex-

¹⁰⁵ Jacobus, D. S., and Bailey, E. G., *Proc. 2nd Intern. Conf. Bituminous Coal*, 2, 241-75 (1928).

¹⁰⁶ Cf. method and results of Gould and Brunjes, ref. 75.

pected to be markedly lower than that of the average ash and, presumably, clinkering in the fuel bed would be aggravated while tube slagging would be minimized. If the reverse condition were true and the fine sizes showed low fusibility, fluxes would be preferentially removed from the fuel bed with a tendency to increased tube slagging and diminished clinkering in the bed.

No correlation of these conclusions with actual experience has been published, and to accept them in the absence of such confirmation may be questionable. It appears that, if the fluxes were segregated so as to produce a considerable quantity of low-fusing slag which tended to drain away before opportunity for solution of more refractory material was afforded, globules of this low-fusing material might well be caught in the stream of combustion gases between fuel particles, where the velocity would be very high, and be carried out of the bed. If, on the other hand, the fluxes were finely divided and intimately mixed with the refractory constituents they would not have the opportunity of forming a fluid slag at so low a temperature and of being carried out of the fuel bed as an upward rain of slag droplets but would remain to flux the refractory ash components and to cause clinker trouble later on.

What actually happens in any particular furnace would appear to depend as much on the equipment, the firing practice, and the coking properties of the coal as on the particle size and distribution of the fluxes. However, studies of the sort made by Moody and Langan may prove to be very valuable if checked against operating experience.

The foregoing remarks were concerned, primarily, with the problems which arise in stoker-fired furnaces. The trend at present in large installations is definitely away

from stoker firing and toward pulverized-fuel firing. In such equipment the rate of ash release is enormous and the bulk of the ash is liberated in the fused condition, although some crystalline material is also released.

Excellent illustrations of the trend of furnace design to meet the severe slagging conditions encountered with this type of combustion were given in a paper by Bailey.¹⁰⁷ A primary furnace separated by a slag screen from a secondary furnace, which contains the boiler tubes, was shown. Much of the slag was caught by the slag screen and dripped back into the primary furnace. Bailey showed that the initial deformation, softening, and fluid temperatures of slag in different parts of the furnace did not correspond to the values found for average ash samples as determined in the laboratory. Segregation took place, the denser ash accumulating at the bottom; the less dense, and generally more refractory, ash at the top. Since water-cooled walls were used in these furnaces the problem was to maintain temperatures high enough so that only a thin layer of slag accumulated on them, the bulk of the slag draining to the bottom, where it was tapped. Since the slag must not become sticky in the course of draining down the walls, ashes with a long fusion range were undesirable. The ideal ash was one that melted sharply so that in cooling the transition from a very fluid state to a dry solid occurred in a short temperature interval.

The study of slag flow in furnaces of this type has been facilitated by means of the motion-picture camera and Kodachrome film. It appears that this and other techniques require to be developed further so that the equilibrium conditions for surfaces covered with molten slag can be estab-

¹⁰⁷ Bailey, E. G., *Trans. Am. Soc. Mech. Engrs.*, **61**, 561-76 (1939).

lished; with a better understanding of the conditions necessary to maintain a thin, evenly flowing film, it will become possible to utilize a wider range of coals in installations of this sort.

It is noteworthy that Bailey retained the conventional terminology, referring to ashes that melt sharply or within a narrow temperature range, although he obviously was thinking of a slag that freezes sharply and has a low viscosity over most of the temperature range within which it is, appreciably, molten. It might be more desirable, from the viewpoint of avoiding any possible confusion in thought, to state explicitly that it is the behavior of a molten slag, both when fluid and on cooling, which is involved.

It appears that the flow curves of slags, described earlier in this survey as a method of test, would provide more useful and detailed information than the softening range determined by the A.S.T.M. standard method, even when it is applied to the slag rather than the ash. However, it would be necessary to take into account the compositional changes occurring in the furnace as the result of the segregation of ash components. It will be recalled that, in the discussion of flow curves, the composition of the ash was shown to have an effect on the viscosity of the resulting slag, on the temperature coefficient of viscosity of this slag, and on its devitrification range. In view of the fact that rather small changes in composition have a pronounced effect upon the behavior of the slag it seems that the application of the procedure to synthetic mixtures within the composition range of coal ashes might make it possible to predict, with some assurance, the behavior of particular ashes in pulverized-fuel furnaces. Likewise the data of Nicholls and Reid⁸¹ should be of value in predicting the type of flow to be anticipated

provided that data on slag composition were available.

THE PROBLEM OF SULFUR AND THE EFFECTS OF ADDING INORGANIC CHEMICALS

The effects of composition of the ash on its fusibility and on the properties of the slag produced by its fusion have been considered in some detail, and the magnitudes of these effects should be kept in mind in reading this section as criteria of what may be expected if the composition of the ash is changed by the addition of inorganic substances to the coal before it is fired. It should also be remembered that to add an inorganic substance to the coal by suspending or dissolving it in water or oil, the two media commonly used for the purpose, and spraying it on the coal provides no assurance that all, or even a large part, of such added substance will remain in the fuel bed to influence the behavior of the ash.

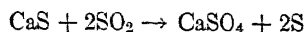
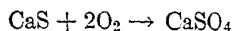
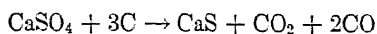
Substances added in considerable proportions, say from 1 to 20 percent of the ash of the coal, can be expected to influence the behavior of the ash to an appreciable extent provided that they, or substances formed from them in the fuel bed, are capable of solution in silicate melts and that they remain in the fuel bed for sufficient time to be dissolved. If they are carried out of the fuel bed they may be expected to influence slag formation on heating surfaces. When, however, the amount of material added is less than 1 percent of the ash present its effect on the fusion of the ash and the properties of the slag will be very small. It is frequently claimed for proprietary mixtures containing components which do not dissolve in silicate melts and which are added in very small amounts that they act as catalysts, although, in general, what reaction is being catalyzed is not made clear. It is important to remember that if a catalyst is to

affect the velocity of reaction between two substances it is necessary for both reactants and the catalyst to be in physical contact with each other and to consider how small is the probability that this condition can exist when the presumptive catalyst is applied to the coal in the ratio of 1 or 2 or even 10 or 20 pounds per ton.

Many of the "treatments" which claim to eliminate or, at least, to mitigate clinker trouble are so inextricably entangled with misconceptions about the role of sulfur in clinker formation that it seems advisable to treat the two topics simultaneously.

Sulfur occurs in coal as a constituent of the organic matter, of sulfates (principally as gypsum), and of iron pyrites and marcasite. Because, for many coals, the principal source of sulfur is the pyritic one, and because, in general, increases in iron content effect a lowering in the softening temperature, there was, for a time, a tendency to associate sulfur with clinkering trouble. Barkley¹⁰⁸ pointed out that there should be no close correlation between clinker trouble and sulfur content.

Iron pyrites on heating decomposes into ferrous sulfide and sulfur. The sulfur vapor released is oxidized to sulfur dioxide or, if catalytic substances are present, to the trioxide. Trifonow¹⁰⁹ has shown that the dioxide will react with calcium oxide, if present, to form calcium sulfite, which at temperatures above 650° C is decomposed to give calcium sulfate and calcium sulfide. Between 650 and 850° both the sulfate and the sulfide are stable but any of the following reactions may occur:

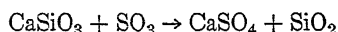


Above 850° C the sulfate and sulfide will react with each other to give the oxides:



At fuel-bed temperatures the end products are calcium oxide and oxides of sulfur, provided that sufficient air is available.

Foerster and Landgraf¹¹⁰ have shown that the trioxide can react with calcium silicate according to the equation



Since calcium sulfate does not dissolve in silicate melts, any sulfur which remains as calcium sulfate during the combustion of the coal functions to prevent the fluxing action of the equivalent calcium oxide with which it is combined and, to this extent, acts as a deterrent to clinker formation, but it will be seen that this effect will be small because the bulk of the calcium sulfate will be decomposed during the combustion process.

The ferrous sulfide which remains from the decomposition of the original pyrites may be oxidized to the sulfate, but the bulk of it actually goes to ferrous or ferric oxide and oxides of sulfur. If this oxidation could be prevented a great deal of the clinkering trouble associated with coals containing large amounts of pyritic iron could be avoided. This is so because, as long as the iron remains as the sulfide, it cannot act as a flux on the refractory ash components present. However, as soon as oxidation to ferrous oxide occurs, fluxing of the kaolin and silica begins.

If the ferrous sulfide remained as such it would give very little trouble because, being a pure compound, it would melt sharply to form a liquid of low viscosity

(1932); *Ann. univ. Sofia, II, Faculté phys.-math.*, 29, 195-9 (1933).

110 Foerster, F., and Landgraf, A., *J. prakt. Chem.*, 134, 1-50 (1932 II).

108 Barkley, J. F., *U. S. Bur. Mines, Tech. Paper* 436 (1928), 7 pp.

109 Trifonow, I., *Brennstoff-Chem.*, 13, 328-9

and high density, insoluble in the silicates present, and would flow quickly down through the fuel bed in small aggregates, giving no trouble. Unfortunately oxidation to ferrous oxide generally occurs, and the attendant evils of a viscous, slowly flowing slag manifest themselves.

These remarks regarding the behavior of pyrites should not be construed as meaning that ferrous sulfide never causes trouble by clinkering on grates. If large pieces of pyrites are present and the conditions are such that molten ferrous sulfide is cooled in the vicinity of the grate it may adhere to the grate and prevent the passage of air through it. If the quantity of pyrites is large, serious erosion of the grates may occur owing to solution of iron from the grate in the molten sulfide. However, coal from a modern preparation plant would be unlikely to contain large amounts of pyrites and certainly not large pieces of this mineral. Coals which contain a large proportion of pyrites undoubtedly cause trouble in hand-fired installations; they can be burned successfully in powdered-fuel furnaces with water-cooled walls.

These statements may appear rather heretical to those holding the view that ferrous sulfide, as such, melts in the furnace to give a viscous troublesome slag, but the following quotation from a paper by Thiesen, Ball, and Grotts⁶⁸ shows that experimental confirmation of the remarks has been obtained.

Iron sulfide is reported to have a melting point of 2,187° F (1,197° C). Since it is a pure compound it was expected to have a sharp melting point and not to exhibit a glue-like viscosity. It was found experimentally that iron sulfide did have such a sharp melting point and that it formed a very fluid liquid, giving the general impression of mercury. Iron sulfide was found to be incompatible with viscous fused compositions in the range of coal-ash compositions. Oxide mix-

tures corresponding to a coal-ash analysis were made up and fused in a clay crucible and heated in an induction furnace. Iron sulfide was introduced either in the cold melt or into the viscous mass, and the viscous mass (2,192° F or 1,200° C) was stirred with a graphite or sillimanite rod. Portions of the melt removed on the end of the rod and cooled showed, on chemical test, that the iron sulfide was distributed in discrete particles throughout the mass. Upon pouring the melt from the crucible, the movement of the viscous silicate melt released to the surface globules of fluid iron sulfide which dropped out to an accompanying shower of sparks. That the globules were iron sulfide and not iron was proved by chemical test. The molten iron sulfide played no part in forming the viscous mass but was itself enclosed in it. The occurrence of iron sulfide in discrete particles was also found in the case of clinker or rather slag, resulting from the combustion of a low-grade, high-pyrite midwestern coal on underfeed stokers. This slag enclosed pieces of coke but was otherwise rather homogeneous in appearance except for exposed corners or protrusions which were vitreous. Analysis showed these vitreous portions to have the same composition as the remainder of the slag and, therefore, to have resulted from rapid cooling. This slag contained, roughly, 0.25 percent sulfide sulfur and 40 percent iron oxide. In general, the slag was very dark gray and microcrystalline. The application of hydrochloric acid to a freshly broken face resulted in the liberation of hydrogen sulfide from points or, rather, very small areas. Gas evolution from the points ceased after a short time. Further exposure of fresh surfaces exposed new sulfide particles. The total sulfide sulfur content of the slag is remarkably low compared to the iron oxide content, the origin of which is largely iron pyrite. The writers hold untenable the view that iron sulfide, derived from pyrite, is an important factor in clinker or honeycomb formation; but rather that the influence of iron pyrites in coal on clinkering is due to the localized increase in iron oxide resulting from its oxidation.

The foregoing appears to indicate that the attempts to improve the clinkering characteristics of coal ash by the removal

of pyritic sulfur are based on a viewpoint which overrates the deleterious effects of ferrous sulfide; however, it should be noted that ferrous sulfide carried out of the fuel bed in the form of fused droplets by the stream of combustion gases will adhere more readily to heating surfaces and furnace walls than ferrous oxide, which melts at 2,516° F whereas ferrous sulfide melts below 2,200° F.

The most extensive investigation of the effect of inorganic chemicals on the burning of solid fuels is that made at the Pittsburgh Experiment Station of the United States Bureau of Mines, where data on the effect of single substances added to the coal were accumulated over a period of many years.¹¹¹ These investigators summed up their experiences in the matter of sulfur as follows:

The only data obtained on sulfur were the amounts retained in the clinker and the ash of the residues from the burnings; the sulfur not thus accounted for passed out with the gases or fly ash. The amount of sulfur in all clinkers was small, ranging from 1 to 5 percent of the total sulfur in the fuel; it was in sulfide form, indicating that particles of sulfide had been buried in the molten slag before they could oxidize. The treatments did not affect the quantity in the slags except that it was slightly greater with heavy treatments of lime, but such increase was not more than 3 percent of the sulfur in the fuel.

Any action of practical importance is more likely to be associated with the deposition of chemicals on the cooler surfaces beyond the furnace and their interaction with the sulfur gases.

In discussing the effects of the various treatments on clinkering in general these authors pointed out that very little, if any, benefit is to be expected. If substances which raised the softening temperature were added, the increase in the total

amount of clinker formed offset any advantage gained, but it was pointed out that, with low-ash coals, the addition of refractory material might be of advantage when the softening temperature is low because such coals give trouble due to insufficient ash to protect the grates from burning and to prevent filling the grate openings with slag. In domestic furnaces operated at low burning rates the accumulation of powdery ash is troublesome, and such ash has a high resistance to the flow of air through the bed. For these reasons these authors considered that the addition of sufficient flux to produce sintering of the ash would be advantageous for such installations.

On the whole, coking was the only property bearing on clinkering of ash which appeared to be significantly influenced by the addition of inorganic substances. This may have some effect on clinker trouble, inasmuch as a strongly coking coal is more likely to produce hot spots in the fuel bed. That inorganic substances may have a very marked influence on the strength and structure of coke is demonstrated by the work of Gauger and Salley,¹¹² who succeeded in producing a pseudocoke by the addition of aluminum salts to a lignite which normally was entirely noncoking.

In this connection, the Bureau of Mines investigators noted that some of their treatments reduced the coking of coal. This effect decreased with decreasing thickness of the fuel bed and, to a lesser extent, with rate of air feed to the fuel bed. These investigators also noted that treatment with water alone generally reduced the coking and to an extent which was related to the amount of water that the coal could absorb in addition to that required to wet the surface. This point is of particular

¹¹¹ Nicholls, P., Rice, W. E., Landry, B. A., and Reid, W. T., *U. S. Bur. Mines, Bull.* 404 (1937), 158 pp.

¹¹² Gauger, A. W., and Salley, D. J., *Proc. 2nd Intern. Conf. Bituminous Coal*, 1, 312-28 (1928).

interest inasmuch as practically all the proprietary preparations sold for treating coal are supposed to be dissolved or dispersed in water as a means for adding them to the coal. This suggests that whatever small effects they have may be due more to the water than to the chemicals added.

Nicholls et al. applied their chemicals to the coal in various proportions, a "light treatment" being 4 pounds per ton, a "heavy treatment" 40 pounds per ton. The effectiveness of the light treatment in reducing coking was appreciable only with one coal and became increasingly negligible as the coking power of the coal increased. On the average, sodium carbonate was most effective, boric acid, molybdenum oxide, and calcium chloride being next and about equal. In some tests they did as well as sodium carbonate. Common salt was much less effective, often having no effect. Potassium chromate and lead nitrate were effective but not used in enough tests to fix their relative positions. Nitric acid equivalent to a heavy treatment was effective, and a light treatment of nitric acid with 4 percent water was more effective than water alone. A heavy treatment with hydrochloric acid was less effective than a heavy treatment with nitric acid.

Nicholls and his coworkers did not investigate the effect of the treatments on slagging of walls and tubes. They pointed out that if the added chemical did not volatilize its action was limited to combination with ash and slag droplets carried out of the bed, but they believed it to be not impossible that some of the chemicals used might have influenced adhesion. They noted that it has been reported that common salt thrown on a fuel bed causes slag to fall from the tubes, but they could present no experimental data to support this statement. This statement has frequently

been made by practical operating men. It seems quite possible that such a procedure might result in sudden fluxing of portions of the slag which would produce mechanical strains resulting in fracture.

In this connection it seems desirable to refer to one proprietary product which has been used extensively and has been said by

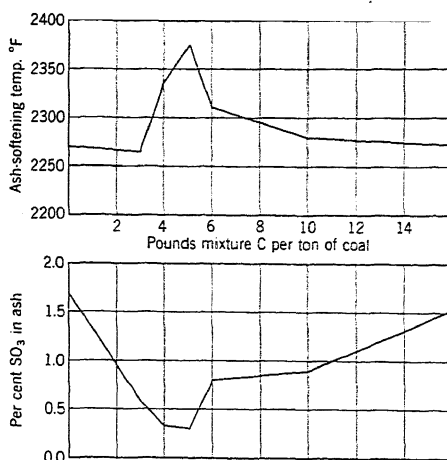


FIG. 23. Effects of adding increasing amounts of proprietary mixture C on the ash-softening temperature and on the percentage of sulfur trioxide in the ash.

many users to have been beneficial in minimizing tube slagging and in giving more satisfactory clinkering characteristics to some coals. The material, which will be called mixture C for convenience, consists principally of calcium chloride with small amounts of manganese dioxide and a dichromate. It is supposed to liberate chlorine at fuel-bed temperatures, and the manganese dioxide and the dichromate are supposed to function as catalysts to accelerate the oxidation of sulfur. In Fig. 23 are shown some of the effects of adding mixture C to a particular coal which had the proximate analysis shown in Table XIII. The percentage ash analysis of the

TABLE XIII

PROXIMATE ANALYSIS OF A PARTICULAR COAL

Moisture, percent	0.78
Volatile content, percent	27.52
Fixed carbon, percent	63.55
Ash, percent	8.15
Sulfur, percent	2.95
Btu (dry)	14,341
Ash-softening temperature	2,270° F

coal was SiO_2 , 31.80; Al_2O_3 , 23.91; Fe_2O_3 , 37.71; TiO_2 , 1.33; CaO , 1.76; MgO , 0.66; $\text{K}_2\text{O} + \text{Na}_2\text{O}$, 1.08; P_2O_5 , 0.17; SO_3 , 1.68.

These data and those shown in the figure were obtained by a private testing laboratory. The method of ashing was unusual. The coal, reduced to 20 mesh, was placed in a muffle furnace maintained at 1,800° F, it being believed that this sudden exposure to a high temperature approximated actual burning conditions more closely than the standard method of ashing. It is to be regretted that complete analyses were not made of the ashes from the treated coal samples instead of only sulfur and ash-softening temperature being determined.

The figure shows a minimum sulfur content in the ash at 5 pounds of mixture C per ton of coal and a maximum in ash-softening temperature at this point. The data may be considered typical. It is in order to inquire whether the reduction in sulfur content of the ash is of any practical significance. Some insight into this may be obtained by the following considerations:

In the first place, the ash of the untreated coal contained 1.68 percent sulfur trioxide according to the usual method of analysis. This corresponds to 0.672 percent of sulfur. It does not seem reasonable to suppose that an ash component present to the extent of slightly more than 0.5 percent could be of any significance in deter-

mining the behavior of the ash as regards clinkering.

In the second place, did the treatment have any considerable effect on sulfur removal during combustion? The ash contained 0.627 percent of sulfur. The coal contained 8.15 percent of ash. The sulfur remaining in the ash of the untreated coal amounts to only 0.0546 percent of the weight of the original coal. The original coal contained 2.95 percent sulfur. Then the percentage of the original sulfur which was not removed during combustion of the coal is 1.85. In short, when the untreated coal was burned, all but 1.85 percent of the sulfur passed out in the stack gases. Similar calculations show that when the coal was treated with 5 pounds of mixture C per ton the sulfur remaining in the ash amounted to only 0.33 percent of that contained in the coal. It seems unreasonable to credit the treatment with having effected any improvement in the coal. When the coal was not treated 98.15 percent of the sulfur passed out in the stack gases. When it was treated 99.67 percent passed out. Certainly if the treatment improved the coal in any way the mechanism by which it did so was not related to its effect on the sulfur. Likewise the effect on the ash-softening temperature is insufficient to account for any improvement.

The foregoing considerations appear to indicate that the treatment was of no significance so far as the alleviation of clinkering and slagging difficulties was concerned, but consider the following statements quoted from a report made by the director of the consulting laboratory in which the above-described tests were made. This report was prepared for a large power company which had retained the laboratory to study the possible value of the treatment.

Observation of the actual effect of the addition to coal of calcium chloride and certain conversion agents shows the formation of friable clinker easily moved on the grate and the tube surfaces were found to be relatively free of slag. Observation was made of the actual operation of a furnace at ——— Company's plant at ———. Analyses of the clinker, tube slag, and fly dust collected on the economizer tubes were also obtained from representative samples of each. The analyses of the cinder show less than 1 percent iron sulfide, while the analyses of the tube slag and economizer deposits show no iron sulfide whatever and less than 1 percent sulfur trioxide; whereas analyses of tube slag in [*sic*] the economizer deposits from installations using untreated coal often show more than 30 percent sulfur trioxide

In contrast to the above it may be said that Nicholls and his coworkers¹¹¹ investigated the effect of chlorine with negative results. However, the sponsors of mixture C state that chlorine alone is ineffective but that the oxides of manganese and chromium catalyze the action of the chlorine.

In spite of the many enthusiastic testimonials by operating men for mixture C and other proprietary compounds there appears to be no convincing evidence that any of them have actually been of value so far as clinkering on grates is concerned. In respect to tube slagging the evidence is, perhaps, not quite so unequivocal, but it remains to be proved that any type of treatment is beneficial.

It appears that the explanation for the enthusiasm displayed by practical men for

certain "treatments" is to be sought in the field of psychology rather than in that of chemistry. If a portion of a shipment of coal is segregated by someone in a supervisory capacity and the fireman is told that the segregated portion is a treated coal or a superior coal it is not unusual for the fireman to obtain much better results (or much worse ones) with the segregated coal than with the rest of the shipment of which it was a part. Frequently the differences may be real and not imaginary, not because the coal was any different, but because the fireman did a better job of firing, if he believed the coal actually to be superior, or a worse one, if he was prejudiced against it. Gutleben¹¹² gave an amusing example of furnace operators who, because they realized that attention was focused on them, obtained results with untreated coal quite as satisfactory as those obtained with treated coal.

A. D. Bailey¹¹⁴ has tested a considerable number of proprietary treating compounds in full-scale equipment without obtaining any evidence of beneficial results. The writer believes that a reading of Bailey's excellent summary will convince any reasonable person that mitigation of slagging troubles is to be sought in the direction of proper design and operation of equipment rather than from any chemical treatment of the fuel.

¹¹² Gutleben, D., *Ind. Eng. Chem., News Ed.*, **16**, 196 (1938).

¹¹⁴ Bailey, A. D., *Trans. Am. Soc. Mech. Engrs.*, **60**, 209-11 (1938).

THE CLEANING OF COAL

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Although chemistry plays only a minor role in the cleaning of coal, the removal of impurities modifies some of its more important chemical and physical properties and hence affects its utilization. The large tonnage of both bituminous and anthracite coal currently cleaned in the United States lends importance to the subject. Cleaning is practiced even more widely in Europe. In 1941, the 460 cleaning plants in the United States produced over 117 million tons of cleaned bituminous coal or about 23 percent of the entire output. The proportion of the annual coal production cleaned mechanically has increased steadily for many years and probably will continue to do so in the future as inferior coal beds are exploited and as the demands of the market become more exacting.

IMPURITIES REMOVABLE BY CLEANING

The impurities with which coal is associated as it comes from the mine are removable only to the extent that they are present in the form of discrete particles

physically detached from the coal and of particle size amenable to cleaning. Shale, clay, sandstone, and bone, which occur as the roof and floor of the coal bed and frequently as bands or partings within the bed, become admixed with the coal in mining. They are frequently the major ash-forming constituents and can largely be removed in the cleaning operation. Often calcite, kaolin, and gypsum are present in the form of thin plates or sheets, principally along vertical fractures and sometimes along bedding planes in the coal; they can be removed only when freed from the coal by breakage on these planes. Pyrite, one of the principal sources of sulfur in coal, is removable if present as discrete particles. Chlorides of sodium, potassium, and calcium are found in some coals, notably those of Great Britain, and are of course partly removed by solution in the cleaning processes employing water. Phosphorus is also removable to some extent, depending on its mode of association.

Finely divided impurities disseminated throughout the coal substance itself are not liberated to an appreciable extent at sizes suitable for cleaning. They therefore re-

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main largely unaffected by ordinary cleaning methods. These impurities include fine silt particles deposited contemporaneously with the coal, the mineral matter in the original plant material from which the coal

The fact that all removable impurities associated with coal are higher in specific gravity than the coal is utilized by nearly all coal-cleaning processes as a means of separating coal and impurity. Coal ranges

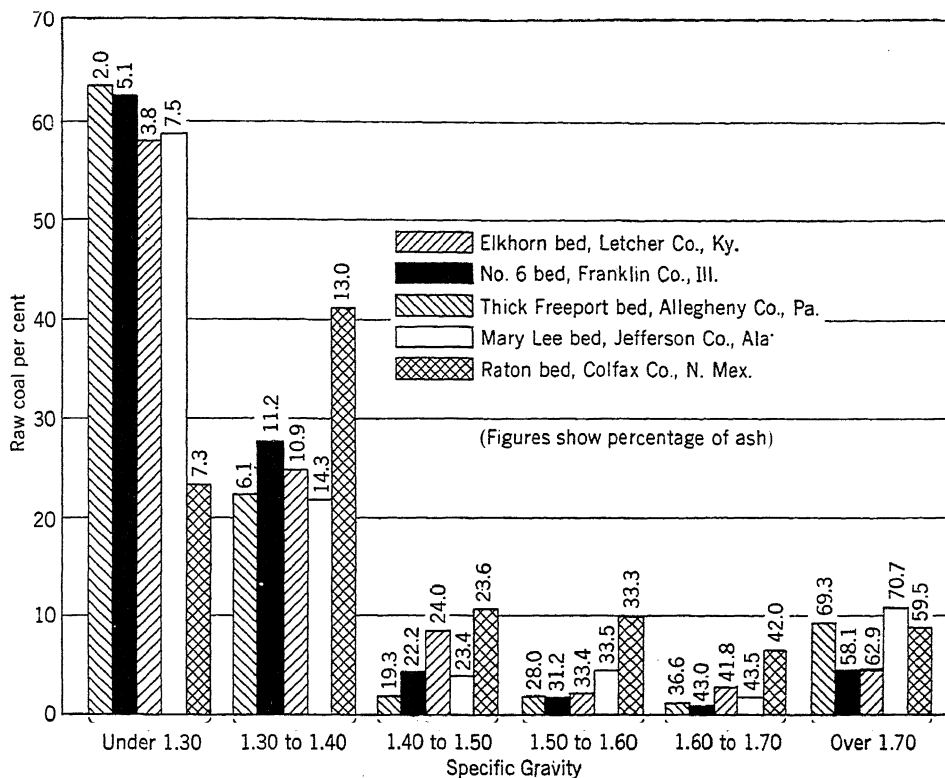


FIG. 1. The specific-gravity composition of several important coals.¹

was derived, finely divided pyrite, organic sulfur and phosphorus, and part of the calcite, kaolin, and gypsum. The combination of these unremovable impurities imposes a fixed or inherent ash, sulfur, and phosphorus content below which a coal cannot be reduced by mechanical cleaning. As each coal differs in the nature and quantity of both removable and unremovable impurities, each has individual cleaning characteristics.

in apparent specific gravity from 1.2 to 1.7, depending on its rank, moisture content, and percentage of ash. Shale, clay, and sandstone range from about 2.0 to 2.6 in specific gravity, depending on their degree of purity; pyrite ranges from 2.4 to 4.9; and calcite and gypsum have a specific gravity of 2.7 and 2.3, respectively. Bony coal and bone are intermediate in specific

¹ Yancey, H. F., and Fraser, T., *U. S. Bur. Mines, Bull.* 300 (1929), 250 pp.

gravity between coal and carbonaceous shale; they range from 1.4 to 2.0.

The cleaning qualities of coals, frequently called washability characteristics, long have been evaluated by specific-gravity analyses made by the float-and-sink method. Such an analysis is generally performed by immersing a sample of the coal in a series of baths of increasing specific gravity and recovering for examination the specific-gravity fractions thus obtained.

Figure 1, taken from a report¹ giving information on the washability characteristics of coals from eleven states, shows graphically the specific-gravity composition of several important coals. The proportion and ash content of the lower-specific-gravity fractions, say those under 1.40, are of principal importance, for they determine the yield and ash content of clean coal obtainable under ideal conditions. Second in significance is the proportion of intermediate-density material—the bony or impure coal; it influences the relative ease or difficulty with which a clean-cut separation can be obtained between coal and impurity in cleaning. The complexity of the cleaning operation and the requirements necessary for a given separation ordinarily increase as the specific gravity corresponding to the desired point of separation becomes lower, both because of smaller differences in average specific gravity between the material to be recovered and that to be rejected and also because of a normal increase in the proportion of particles near in specific gravity to the point of separation. A method of interpreting specific-gravity composition in terms of washability has been described by Bird,² and more recently by Coe.³ Reasonably complete information on washability characteristics

is available for the coals of Alabama and Washington⁴ and those of Illinois.⁵

COAL-CLEANING PROCESSES

All coal-cleaning processes in general use are gravity-concentration methods, but methods based upon surface and magnetic properties and upon electrical conductivity, sliding friction, and strength, although of minor significance, are sometimes employed. The important processes are grouped according to type in the following classification:

- I. Gravity stratification.
 - A. Wet processes.
 1. Jigs.
 2. Launderers.
 3. Upward-current classifiers.
 4. Heavy mediums.
 - (a) High-density suspensions.
 - (b) High-density solutions.
 5. Tables.
 - B. Dry processes.
 1. Pneumatic tables.
 2. Air jigs.
 3. Air-sand.
- II. Nongravity processes.
 1. Froth flotation.

As most of these processes have been described in textbooks⁶ on coal cleaning,

⁴ Bird, B. M., Gandrud, B. W., et al., *U. S. Bur. Mines, Repts. Investigations* **3012** (1930), 12 pp., **3014** (1930), 17 pp., **3067** (1931), 24 pp., **3083** (1931), 12 pp., **3157** (1932), 28 pp., **3170** (1932), 14 pp., **3200** (1933), 10 pp., **3204** (1933), 15 pp., **3206** (1933), 9 pp., **3315** (1936), 23 pp., **3449** (1939), 12 pp., **3450** (1939), 12 pp., and **3458** (1939), 12 pp.; *Univ. Wash. Eng. Expt. Sta., Bull.* **28** (1924), 231 pp.

⁵ Fraser, T., and Yancey, H. F., *U. S. Bur. Mines, Tech. Paper* **361** (1925), 23 pp. Mitchell, D. R., *Univ. Illinois Eng. Expt. Sta., Bull.* **258** (1933), 44 pp. McCabe, L. C., Mitchell, D. R., and Cady, G. H., *Illinois State Geol. Survey, Rept. Investigations* **34** (1934), 61 pp. Mitchell, D. R., and McCabe, L. C., *ibid.*, **48** (1937), 84 pp.

⁶ Prochaska, E., *Coal Washing*, McGraw-Hill Book Co., New York, 1921, 382 pp. Chapman, W. R., and Mott, R. A., *The Cleaning of Coal*, Chapman and Hall, London, 1928, 680 pp. Louis, H., *The Preparation of Coal for the Market*, Methuen and Co., London, 1928, 217 pp. Minl-

² Bird, B. M., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 82-111 (1928).

³ Coe, G. D., *U. S. Bur. Mines, Circ.* **7045** (1938), 10 pp.

in the following brief description references are given only for the more recent processes and to articles of specific interest.

Jigs. Jigs, which are among the oldest forms of concentrating devices, remain the most popular single type of equipment for cleaning bituminous coal. In jigging, a bed of coal resting on a perforated surface is subjected to the action of periodic upward and downward currents of water. This action causes stratification of the coal and impurity, principally according to their respective specific gravities, but also by the size and shape of particle. Owing to its lower specific gravity and consequent lower settling rate, the coal is concentrated largely in the upper strata of the bed, while the impurity, with its higher specific gravity and greater settling rate, accumulates in the lower strata.

In the Baum-type jig illustrated in Fig. 2 the water pulsations are created by alternately admitting and releasing compressed air above the surface of the water in chambers adjoining the washing compartment. Other common types of jigs utilize reciprocating plungers or diaphragms to produce the water pulsations. Jigs are employed to clean either sized or unsized coal and in a few instances to treat in one operation all sizes from dust up to 6 or even 8 inches. With such a wide size range the cleaned product may meet the market requirements, but the efficiency with which some of the sizes are treated is necessarily decreased. Capacities of as much as 500 tons per hour are obtained.

Launders. Launderers of the Rheolaveur type illustrated in Fig. 3 are widely used

to wash bituminous coal and less commonly anthracite. The Rheolaveur system consists essentially of one or more launders or troughs in which the coal and impurity particles are separated by alluviation.⁷ As the material is moved along the slightly inclined launder the heavier impurities tend to settle into the lower strata of the bed, the lighter coal remaining in the upper strata and overflowing at the end of the launder. The refuse accumulating in the bottom is removed continuously through special valves called rheo boxes, which may or may not be supplied with an upward current of water to prevent the discharge of coal.

In operation, all sizes of coal from dust up to about 4 inches frequently are washed in a coarse-coal launder of the sealed-discharge type, and the material finer than about $\frac{3}{8}$ inch is screened from the washed coal for recleaning in fine-coal launders of free-discharge type if further treatment is required. An alternative procedure is to screen the coal before washing and treat each size separately. Each coarse-coal launder is provided with several rheo boxes for the removal of refuse and middlings, but the products from all but one box are recirculated in the launder to insure more complete cleaning. This recirculation of middlings material is a distinctive feature of the Rheolaveur system. Launderers for washing fine coal are frequently operated as a group of four superimposed one above another, the rheo boxes in the upper launders discharging incompletely separated material by gravity to the lower launders for further treatment. The two upper launders thus act as a primary unit to produce finished washed coal and a product that is separated in the lower launders into a final refuse and a middlings for recircu-

kin, R. C. R., *Modern Coal-Washing Practice*, Ernest Benn, London, 1928, 310 pp. Berthelot, Ch., *Épuration, séchage, agglomération, et broyage du charbon*, Dunod, Paris, 1938, 393 pp. Mitchell, D. R., Editor, *Coal Preparation*, Am. Inst. Mining Met. Engrs., New York, 1943, 720 pp.

⁷ Gilbert, G. K., *U. S. Geol. Survey, Professional Paper 86* (1914), 263 pp.

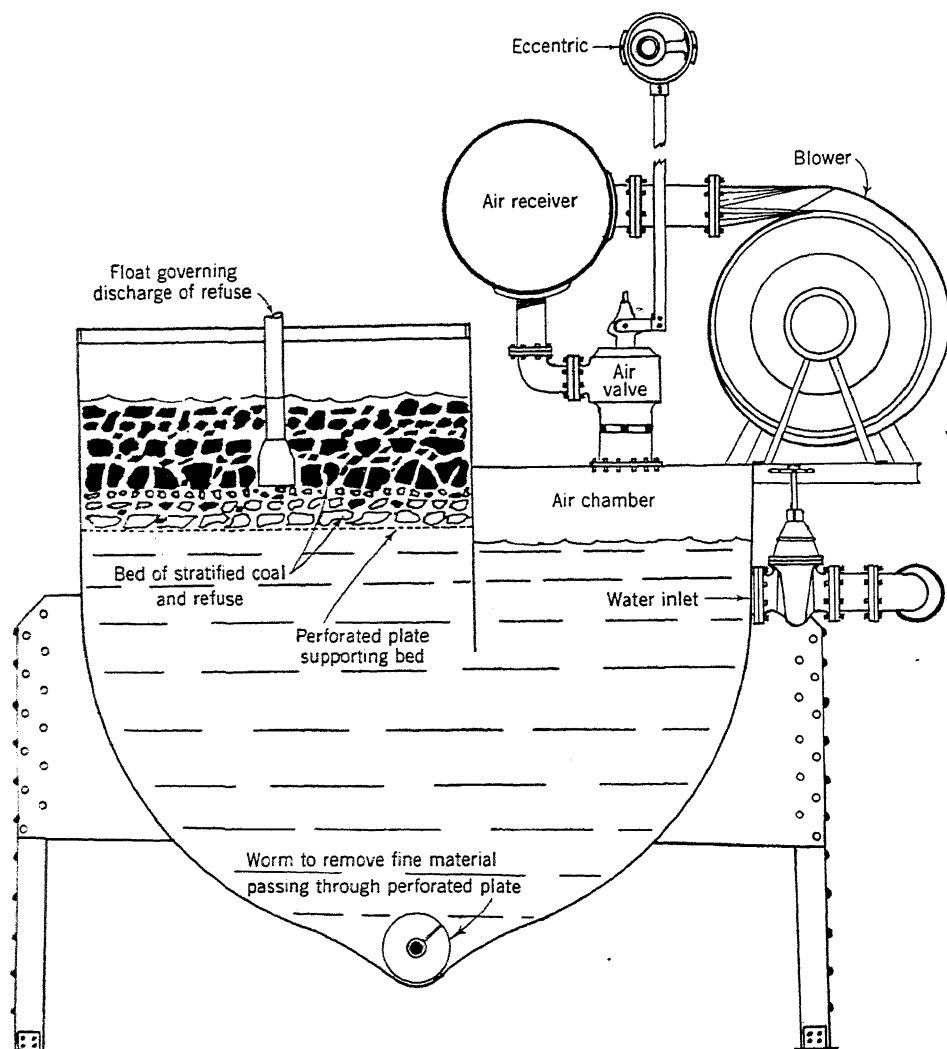


FIG. 2. Baum-type jig.

lation. The capacity of the Rheolaveur system is variable, depending on the width of launder and the size of the feed, whether coarse or fine. Coarse coal is treated at rates ranging from 65 to 250 tons an hour, and fine coal at rates as low as 20.

Upward-Current Classifiers. Upward-current classifiers are used for cleaning an-

thracite and, less frequently, bituminous coal. They differ from jigs primarily in that they employ a continuous rather than a pulsating current of water. This continuous upward current of water has a velocity between the terminal velocity of fall of coal particles and that of impurity particles. The coal particles, having a

velocity of fall less than the velocity of the rising current, are carried upward and discharged with the water, while the more rapidly falling particles of refuse settle

coals, is employed for egg, nut, and pea sizes rather than for the wide range of sizes generally treated in jigs.

In the Menzies Cone⁸ and Hydrotator⁹

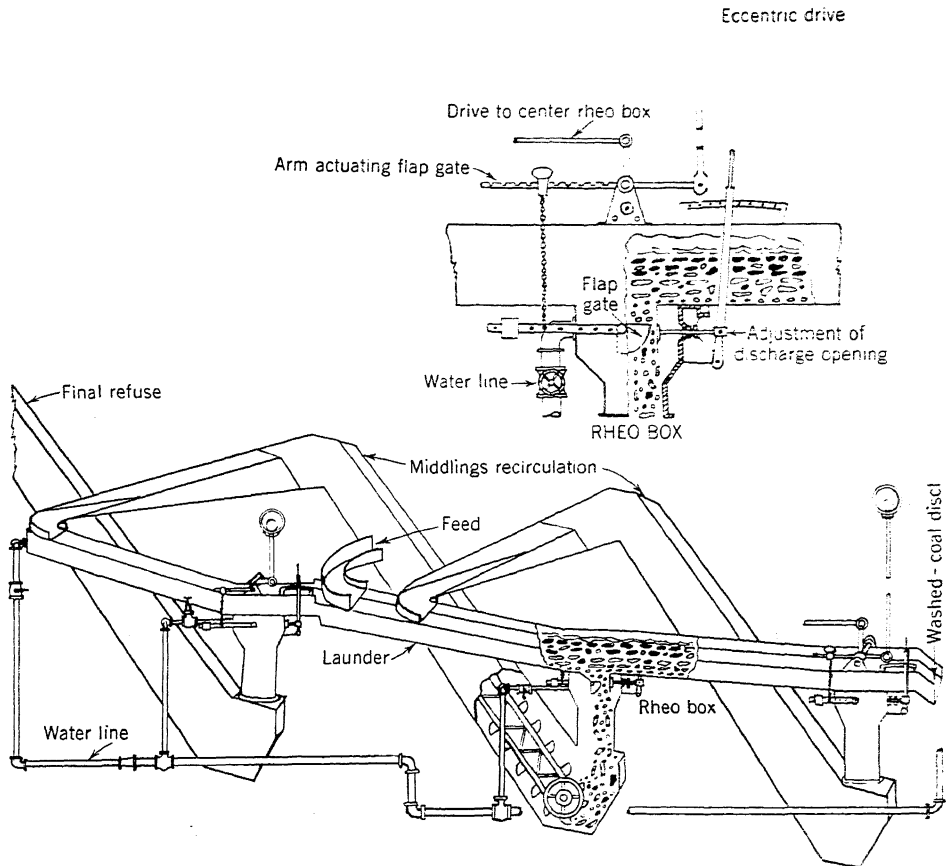


FIG. 3. Rheolaveur-type launder.

downward through the rising stream and are removed at a lower level. However, as the velocity with which a body falls through a fluid medium is determined by its size as well as by its specific gravity, classifiers ordinarily can be used to clean only a restricted range of sizes in one operation. For example, the Hydro-Separator, which is used primarily to clean bituminous

classifiers, used largely for anthracite, the classifying effect of the upward water current is assisted to some extent by the action of particles of bony or impure coal

⁸ Anon., *Coal Age*, 26, 188-9 (1924); Fraser, T., *Modern Mining*, 5, 119-28 (1928).

⁹ Remick, W. L., *Trans. Am. Inst. Mining Met. Engrs.*, 75, 569-79 (1927). Remick, W. L., and Jones, G. B., *Am. Inst. Mining Met. Engrs., Tech. Pub.*, 219 (1929), 12 pp.

of intermediate density held in suspension by the water current. The suspended material increases the effective specific gravity of the water and thus aids the separation. Classifiers of the Menzies type are used to clean the various standard sizes of anthracite from egg to No. 4 buckwheat, $\frac{3}{32}$ to $\frac{3}{64}$ inch, and the Hydrotator for the smaller sizes only. In practice, several commercial sizes of coal may be cleaned together in a single classifier, and a capacity of as much as 150 tons an hour is obtained with the coarser sizes.

Heavy-Medium Processes. The beneficial effect obtained from solids suspended in the washing water in some types of upward-current classifiers previously mentioned is utilized in high-density suspension processes of washing coal. These processes employ either an unstable or a semistable suspension of a finely divided solid material, usually one foreign to the coal, to create a bath having an effective specific gravity greater than that of coal but less than that of impurity. Thus, in effect, a float-and-sink type of separation between coal and impurity is simulated. However, in those processes in which a rising current of water is required to maintain the suspension and assist in the separation, size as well as specific gravity influences the separation. Size, however, is less important with these processes than with those previously described, because as the density of the medium increases the velocity of rising current required decreases, and consequently the separation according to particle size is minimized. Verdinne¹⁰ has described the various heavy-medium processes, and Cummings¹¹ presented a critical comparison of them.

¹⁰ Verdinne, H., *Ann. mines Belg.*, **40**, 431-72 (1939); *Colliery Guardian*, **159**, 667-70, 711-15, 747-50, 787-8 (1939). Mott, R. A., *J. Inst. Fuel*, **9**, 158-70 (1936).

The Chance method,¹² illustrated in Fig. 4, is the most widely used of the high-density suspension processes; it was originally developed and is still used principally for anthracite in the United States but has been applied to the cleaning of bituminous coal at a number of plants. In this method the suspended solid is sand, with a grain size of 0.2 to 0.5 millimeter. As sand of this size settles rapidly the bath is agitated mechanically and by upward currents of water admitted at several levels in the cone. An effective specific gravity up to 1.65 can be obtained, and a capacity reaching 600 tons an hour is possible with bituminous coal. Coal ranging in size from 10 inches to $\frac{1}{4}$ or $\frac{1}{16}$ inch can be cleaned in one operation by the Chance process; but, as in other high-density suspension methods, the fine sizes cannot be treated because they decrease the density of the medium and cannot be recovered from the sand by screening.

The Barvoys process,¹³ also known as the de Vooy's, barite, or Sophia-Jacoba process, was installed at twenty-one plants in England and on the Continent between 1931 and 1939 but is not used in the United States. A suspension of barite (BaSO_4 , specific gravity 4.2) is the separating medium utilized in this method. The suspension is stabilized by the addition of 2 volumes of clay per volume of barite. With this addition of clay the suspension is said to be stable in the range from 1.30 to 1.60 specific gravity, but at the Sophia-Jacoba plant the separating bath is heated to 90° F to reduce its viscosity to an ac-

¹¹ Cummings, A. D., *Colliery Guardian*, **161**, 436-8 (1940).

¹² McLaughlin, J. T., *Trans. Am. Inst. Mining Met. Engrs.*, **94**, 324-31 (1931). Bird, B. M., *Mechanization*, **2**, No. 6, 46-52 (1938).

¹³ Gruppel, K., *Glückauf*, **70**, 429-35 (1934). Anon., *Colliery Guardian*, **161**, 347-51 (1940).

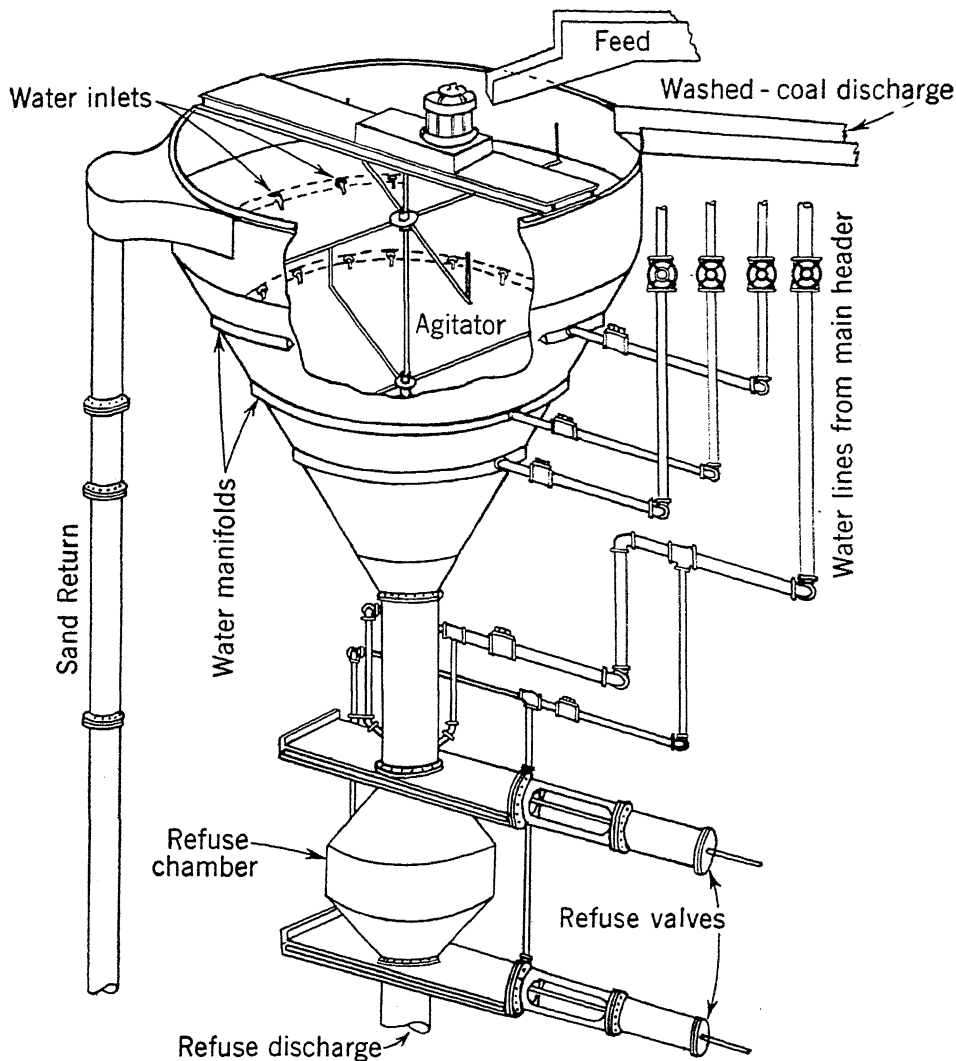


FIG. 4. Chance cone.

ceptable value. Heating is not mentioned in descriptions of other plants. The process was originally used for coal ranging in size from $3\frac{1}{4}$ inches to $\frac{3}{16}$ inch at a capacity of 200 tons an hour; coal up to 8 inches in size is treated in the more recent plants. Although coal less than $\frac{3}{16}$

inch in size is not treated by the process, fine coal resulting from degradation of the larger pieces contaminates the suspension and is therefore removed from the barite and clay by froth flotation. The barite and clay are recovered for reuse by sedimentation in a Dorr-type thickener.

In the Tromp¹⁴ process developed at the Domaniale mine, Kerkrade, Netherlands, in 1936 and employed at two plants in England, the suspension is either magnetite or sintered pyrite ground through 100-mesh. The unique feature of the Tromp method is that the tendency of the unstable suspension to settle in the washing chamber is utilized rather than prevented, as in other processes employing unstable suspensions. Owing to settling of the magnetite, the specific gravity of the bath increases from top to bottom; in the original installation the range in specific gravity was from 1.53 at the top of the bath to 1.83 at the bottom. In operation, the clean coal floats at the surface of the suspension and is skimmed off, while the refuse sinks through the bath and is discharged at the bottom. Bony or impure coal intermediate in specific gravity between that of the top of the bath and that of the bottom can neither float nor sink and therefore remains suspended within the bath. It is removed continuously by a gently horizontal cross flow of the medium, which carries it to an elevator for disposal.

The Tromp method is thus especially well suited to making three or even more products, that is, a high-ash middling in addition to the primary washed coal and refuse. This feature is particularly useful if the coal is unusually hard to clean, that is, if it contains considerable middlings, or if an especially low-ash washed coal is required. The process has been successful for cleaning coal sized between $3\frac{1}{4}$ inches and $\frac{1}{4}$ inch, and extension of this size range to $\frac{1}{8}$ inch is anticipated.

¹⁴ Schäfer, O., *Glückauf*, **74**, 451-6 (1938); *Colliery Guardian*, **157**, 1073-7 (1938). Moser, H., *Z. Ver. deut. Ing.*, **83**, 53-7 (1939). Holmes, C. W. H., *Colliery Guardian*, **159**, 861-4, 899-902 (1939).

The Loess¹⁵ process, developed at the state mines, in the Netherlands, differs from the similar processes largely in the suspension. The suspension employs loess, a wind-sorted, sandy clay earth of wide geographical distribution. Loess of the type used in the process has a size distribution of 75 percent between 100 and 20 microns and 25 percent finer than 20 microns. The loess forms a suspension which, in the range from 1.25 to 1.65 specific gravity, is stable enough at the concentration required in the separating bath to be used without special means of agitation, but which can be recovered from the dilute suspension in the rinsing water readily for reuse because of its freedom from slimes. Coal of sizes down to 8 millimeters has been treated.

A similar process, known as the Wuensch cone method, was formerly employed at a mine in Kansas. The suspended material in the cone, however, was from a bed of clay underlying the coal. With ferrosilicon or galena as the suspended solid, the Wuensch or M.B.I.¹⁶ process is employed in the treatment of ores.

Table I, which summarizes the characteristics of the several high-density suspension processes for cleaning coal, was compiled from the reports by Verdinne,¹⁰ Cummings,¹¹ and Driessen.¹⁵

The use of solutions of high specific gravity, as distinguished from dense suspensions, to form a separating bath for cleaning coal has been attempted from time to time, but with only limited industrial success. An aqueous solution of cal-

¹⁵ Driessen, M. G., *J. Inst. Fuel*, **12**, 327-41 (1939); *Colliery Guardian*, **158**, 783-8, 832-3 (1939).

¹⁶ *The M.B.I. (Wuensch) Process*, American Zinc, Lead, and Smelting Co., 1940, 34 pp. DeVaney, F. D., and Shelton, S. M., *U. S. Bur. Mines, Rept. Investigations 3469-R* (1940), 25 pp.

TABLE I

CHARACTERISTICS OF HIGH-DENSITY-SUSPENSION COAL-WASHING PROCESSES

Characteristic	Process			
	Chance	Barvoys	Tromp	Loess
Solid in suspension	Sand	Barite and clay	Magnetite	Loess
Average particle size of solid, inch		$\frac{1}{1000}$	$\frac{1}{800}$	$\frac{1}{600}$
Agitation	Upward currents and mechanical	None	None	None
Effective specific gravity	1.35 to 1.65	1.30 to 1.55	1.40 to 1.80	1.25 to 1.65
Means of separating middlings from refuse	None	Upward current of suspension in separate bath	Cross currents of several densities in bath	Upward current of suspension in separate bath
Minimum size treated, inch	$\frac{1}{16}$	$\frac{3}{16}$		$\frac{3}{16}$

cium chloride is used in the Lessing,¹⁷ Fuel Process Co., and Ougrée-Marihaye¹¹ processes. The Fuel Process Co. method, which is employed at a number of plants in the United States for cleaning egg and nut sizes, uses calcium chloride solution of approximately 1.2 specific gravity. Upward currents produced by mechanical agitation allow a higher effective specific gravity to be attained. The fact that only a comparatively low density can be obtained, and the expense entailed by the loss of calcium chloride entrained in the washed coal and refuse products, limit the application of these processes to coarser sizes of coal.

The first limitation has been eliminated in the du Pont¹⁸ process employed for

treating anthracite at one plant in Pennsylvania. Halogenated hydrocarbons—such as tetrabromoethane (specific gravity 2.964), pentachloroethane (specific gravity 1.678), and trichloroethylene (specific gravity 1.462), or mixtures of any two of these compounds in the proportions required to give the desired specific gravity—constitute the separating medium. Loss of the medium through adsorption by the coal and refuse is minimized by preliminary treatment of the raw coal with a so-called active agent. The active agent is a surface-active substance which, with water, forms a protective film around the individual particles of coal and thus prevents adsorption of the heavy medium. Starch acetate or tannic acid in concentrations of 0.01 percent are satisfactory active agents.

All portions of the du Pont equipment in which the separating medium is used or circulated must be vapor-sealed, to prevent loss of the medium and because the medium is toxic. The medium is recovered for reuse by settling and distillation. Like the other dense-medium processes, the du Pont system is not suited to cleaning coal of the finer sizes.

¹⁷ Lessing, R., *J. Inst. Fuel*, **2**, 5 (1928); *Proc. 2nd. Intern. Conf. Bituminous Coal*, **2**, 1-21 (1928); *Fuel*, **9**, 20-9 (1930). Bertrand, M. G., *J. Inst. Fuel*, **8**, 328-42 (1935).

¹⁸ Foulke, W. B., *Coal Age*, **43**, No. 5, 74-9 (1938); *Eng. Mining J.*, **139**, No. 5, 33-9, 48 (1938). *Coal Age*, **45**, No. 11, 37-9 (1940). Foulke, W. B., U. S. Pat. 2,150,918 (1939). Alexander, H. L., du Pont, H. I., and Foulke, W. B., U. S. Pats. 2,150,899, 2,151,578 (1939). Foulke, W. B., and Greager, O. H., U. S. Pat. 2,208,758 (1940). Foulke, W. B., and Willis, W. A., U. S. Pat. 2,150,917 (1939). Alexander, H. L., and Foulke, W. B., U. S. Pat. 2,193,957 (1940).

The development of other high-density solutions having the advantages of these halogenated hydrocarbons but not their disadvantages, namely, comparatively high cost, volatility, and toxicity, is a field of research in which chemical technology may make a significant contribution to the art of cleaning coal.

Tables. Tables have long been used for cleaning coal of the finer sizes. All sizes from dust up to $\frac{3}{4}$ inch and occasionally up to 1 inch or larger are treated. A table consists essentially of a rectangular deck provided with numerous parallel, longitudinal riffles or barriers. The deck is reciprocated longitudinally with a differential motion in a nearly horizontal plane. Coal and impurity particles fed to the table are acted upon by three forces: that of gravity, that imposed by the motion of the deck, and that applied by a flow of water across the deck perpendicular to the direction of the riffling. The coal and impurity particles stratify principally according to specific gravity in the spaces between the riffles, the impurity on the bottom next to the surface of the deck and the coal particles superimposed. The motion of the table moves the material forward along the riffles toward the refuse-discharge end of the table; the impurity, being in direct contact with the deck, is moved forward more rapidly than the coal. Concurrently, the cross flow of water washes the superimposed coal over the riffles toward the coal-discharge edge of the table.

Pneumatic Processes. All the cleaning processes described thus far involve wetting the coal with water. As the drying of the finer coal preparatory to use is costly, coal of the small sizes is sometimes cleaned by pneumatic methods. About 15 percent of the coal cleaned in the United States in 1941 was so treated.

The air table, like its counterpart the wet coal-washing table, is essentially a reciprocating riffled deck. Air currents rising through the perforated deck create a mobile condition in the bed of coal and promote stratification of the coal and impurity particles between the riffles. The impurity particles are transported longitudinally along the riffles to the end of the table by the reciprocating motion, while the lighter coal particles, buoyed up by the air currents, pass transversely across the riffles, where they are discharged along the side of the table.

The Stump air-flow¹⁹ cleaner operates much the same as a jig, except that the upward pulsations utilized for stratification of the coal and impurity particles are due to air rather than water. Units of this type are designed to treat sized coal up to a maximum of 3 inches, or slack coal including the finest dust. In general, pneumatic processes treating unsized feeds are less efficient in separating coal and impurity than wet processes employing similar equipment.

In the air-sand²⁰ process a bed of dry sand, fluidized by a continuous upward flow of air introduced through a porous bottom, is employed as the separating medium. The mixture of sand and air simulates a dense liquid on which the coal floats and the impurity sinks. Coal ranging in size from 3 inches to $\frac{1}{4}$ inch is treated at rates as high as 85 tons per hour.

Froth Flotation. The flotation process for cleaning coal, as distinguished from heavy-medium methods sometimes erroneously referred to as flotation processes, has been used sporadically at only a few wash-

¹⁹ Davis, D. H., and Hanson, V. D., *Mining Cong. J.*, 25, No. 5, 10-6 (1939).

²⁰ Beddow, W. W., *Coal Age*, 41, 139-44 (1936).

eries in the United States but is employed extensively in Europe. In Great Britain alone, over 2 million tons of coal was cleaned by flotation in 1938. It is one of the few coal-cleaning processes in which the separation is not based upon specific gravity. The process depends upon differences in wettability; the surface of coal is wetted less readily by water than are those of its impurities.

Froth flotation,²¹ briefly described, involves agitating coal $\frac{1}{10}$ inch or finer in size with 4 to 10 times its weight of water and a quantity of reagent, usually amounting to less than 0.25 percent of the weight of the coal. The reagent, together with air, forms a froth to the bubbles of which coal particles selectively attach themselves and are buoyed up to the surface, where they may be removed. The impurity particles are wetted by the water, therefore remain below the surface, and can thus be separated from the coal. The flotation machines generally used are of pneumatic or mechanical type, according to whether compressed air or a revolving impeller is employed to secure agitation and the formation of bubbles. Information on the flotation of coal at European washeries, including types of machines used, reagents and their consumption, performance, and cost data, was summarized by Mayer.²²

The Elmore vacuum-flotation process²³ is used to a limited extent in Europe for cleaning fine coal. A mixture of coal, water, and suitable reagent, usually a paraffin or fuel oil, is introduced into a vacuum chamber, where the air dissolved in the water and that entrained in the mixture

are liberated in the form of bubbles to create a froth. The advantages claimed are that the power required to produce the vacuum is less than the power necessary for mechanical agitation and that the froth obtained is less stable and hence more easily dewatered. The Trent process,²⁴ developed during the World War of 1914-18 but since discarded, is not actually a flotation method but involves similar physical principles. Coal passing 100-mesh is suspended in water and mixed with an oil or other organic liquid immiscible with water, amounting to 30 or 40 percent of the weight of the coal. The oil displaces the water film from the surface of the coal, and together they form a pasty agglomerate that can be separated from the water and the water-wetted impurities by screening.

The comparatively high cost of flotation has limited its application to coal cleaning. Flotation has several appealing technical advantages, however, that eventually may bring it into greater use. Chief among them is the fact that it is suited to cleaning coal of the finer sizes which cannot be treated as effectively by most other cleaning processes. A second advantage is that by choice of suitable reagents and operating technique the wettability and hence flotation of the various components of a coal can be controlled, permitting greater flexibility in operation and allowing the coal to be separated into three or more products. The chemical aspects of flotation are discussed in a subsequent section.

PERFORMANCE OF CLEANING PROCESSES

The ideal cleaning process, from the standpoint of performance, would be one

²¹ Yancey, H. F., and Taylor, J. A., *U. S. Bur. Mines, Circ. 6714* (1935), 29 pp.

²² Mayer, E. W., *Coal Age*, **38**, 375-9 (1933).

²³ Dept. Sci. Ind. Research, *Fuel Research Board Rept.*, **1931**, pp. 57-8; *ibid.*, **1932**, pp. 23-5. Anon., *Colliery Guardian*, **149**, 104 (1934).

²⁴ Perrott, G. St. J., and Kinney, S. P., *U. S. Bur. Mines, Rept. Investigations 2263* (1921), 18 pp.; *Chem. Met. Eng.*, **25**, 182-8 (1921). Ralston, O. C., *Coal Age*, **22**, 911-4 (1922).

in which all coal lower in specific gravity than a predetermined value, the specific gravity of separation, would be recovered in the cleaned product and all material of higher specific gravity would be rejected as refuse. No cleaning process achieves this goal. The type of separation between coal and impurity actually accomplished

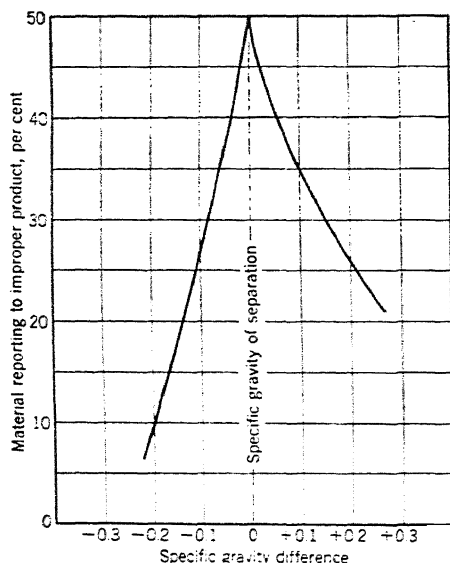


FIG. 5. Typical separation between coal and impurity accomplished in practice.²⁵

is illustrated graphically in Fig. 5.²⁵ Coal of low density and impurity of high density report largely to their proper products—washed coal and refuse, respectively; but, as the specific gravity of separation is approached, the proportion of material reporting to an improper product increases rapidly. The shape of the curve suggests that some type of probability function relates the proportion of material reporting to an improper product with the difference between its specific gravity and that of the

point of separation. Tromp,²⁶ observing that the shape of the curve is similar to that of a Gaussian error distribution curve, was able to derive a formula to express the relationship mathematically.

Imperfect separation of the materials of intermediate density, as illustrated in Fig. 5, is characteristic to some degree of all gravity coal-washing processes, regardless of their mode of operation. It can be ascribed largely to the inherent difficulty of stratifying materials differing only slightly in density, but it is attributable also to the effects of the two factors, particle size and particle shape. Size and shape modify density in all cleaning processes employing currents of a fluid, whether the fluid is water, air, or a high-density suspension, because the size and shape of a particle, as well as its density, determine its motion in the moving fluid.

The influence of particle size is especially pronounced with the wet coal-washing table.²⁷ In general, the size of the particles of a given density discharged from the table become successively finer with increasing distance from the mechanism end of the table. At any given point of discharge, fine particles of one density are accompanied by coarser particles of higher density. Thus the wet table operates most efficiently with a coal in which the average particle size of the impurity is finer than that of the clean coal.

With the pneumatic table, the effect of particle size is reversed.²⁸ The size of the particles of given density discharged from

²⁶ Tromp, K. F., *Glückauf*, **73**, 125-31, 151-6 (1937); *Colliery Guardian*, **154**, 955-9, 1009 (1937). Terra, A., *Rev. ind. minérale*, **446**, 409-13 (1939).

²⁷ Bird, B. M., *U. S. Bur. Mines, Rept. Investigations* **2755** (1926), 8 pp.

²⁸ Taggart, A. F., and Lechmere-Oertel, R. L., *Trans. Am. Inst. Mining Met. Engrs.*, **87**, 155-212 (1930). Yancey, H. F., and Porter, C. B., *U. S. Bur. Mines, Tech. Paper* **536** (1932), 18 pp.

²⁵ Yancey, H. F., Geer, M. R., and Shinkoskey, R. E., *U. S. Bur. Mines, Rept. Investigations* **3372** (1935), 19 pp.

the table becomes successively coarser with increasing distance from the mechanism end of the table, and, at any given point of discharge, coarse coal is accompanied by finer impurity; thus the pneumatic table can make a more efficient separation when the average particle size of the impurity is coarser than that of the coal.

Particle shape likewise has opposite effects with the two types of tables.²⁹ With the wet table the tendency of the impurities to be flakier than the coal assists in the separation of coal and refuse, because flaky particles tend to move toward the refuse end of the table. But with the pneumatic table, flaky particles tend to be discharged with the clean coal, and thus the separation of flaky refuse particles is more difficult.

It is the difference in the direction of the fluid currents that makes the particle size and shape have opposite effects with the two types of tables. With the wet table, the flow of water is transverse and nearly horizontal; with the pneumatic table, the flow of air is vertical.

Size of particle is similarly important in the operation of jigs, for it as well as density influences the stratification obtained with the pulsating currents of water.³⁰ For example, in an investigation treating a coal ranging in size from 3 inches to zero, the efficiency of the separation was shown to be higher for the intermediate sizes than for either the coarser or finer sizes; moreover, the finer sizes were separated into coal and refuse at lower density than the coarser sizes.³¹ That particle shape is a factor in jigging is illustrated by the necessity of employing a stronger suction stroke

to remove flaky material of intermediate or even high density.³²

The effect of particle size can be observed in performance data of Rheolaveur washers. As pointed out by Crawford and coworkers, a separation according to particle size, in addition to that by density, occurs when the material in the launder is thick and sluggish. In the new Battelle launder described by Richardson greater mobility in the bed is achieved by vertical currents of water supplied through perforated plates forming the bottom of the launder.³³

Detailed information on the effect of size and shape of particles with other types of cleaning processes is not available. Probably, however, the only processes in which size and shape are not important factors are those dense-medium methods in which no upward current of the separating medium is employed.

Imperfect treatment of the materials near in density to the point of separation manifestly influences the quality of the cleaned coal and refuse produced in the cleaning operation. The magnitude of this influence depends on the proportion of such material present, which in turn is determined by the specific-gravity composition of the coal, and on the specific gravity at which the separation between coal and impurity is made.

Owing to the wide variation in the quantity and ash content of the inherent and removable impurities in coal, no adequate generalization can be made regarding the reduction in percentage of ash obtainable in cleaning. Some coals can be reduced

²⁹ Bird, B. M., Gandrud, B. W., and Nelson, E. B., *ibid.*, **3012** (1930), 13 pp.

²⁹ Yancey, H. F., *Trans. Am. Inst. Mining Met. Engrs.*, **94**, 355-68 (1931).

³⁰ Yancey, H. F., and Fraser, T., *ibid.*, **71**, 1079-87 (1925).

³¹ Yancey, H. F., and Geer, M. R., *U. S. Bur. Mines, Rept. Investigations* **3371** (1938), 18 pp.

³² Bird, B. M., Gandrud, B. W., and Nelson, E. B., *ibid.*, **3012** (1930), 13 pp.

³³ Crawford, J. T., Proctor, C. P., and Williams, M. J., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 172-88 (1938). Richardson, A. C., *ibid.*, **130**, 156-70 (1938). Crawford, J. T., Proctor, C. P., and Younkins, J. A., *ibid.*, **139**, 269-87

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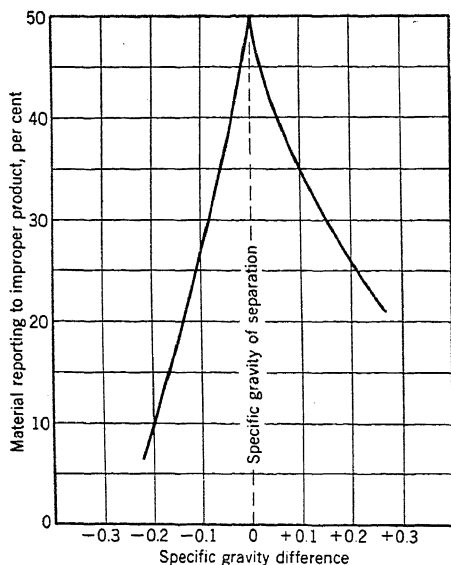


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²⁹ Yancey, H. F., *Trans. Am. Inst. Mining Met. Engrs.*, **94**, 355-68 (1931).

³⁰ Yancey, H. F., and Fraser, T., *ibid.*, **71**, 1079-87 (1925).

³¹ Yancey, H. F., and Geer, M. R., *U. S. Bur. Mines, Rept. Investigations* **3371** (1938), 18 pp.

readily to 5 percent or less of ash; others cannot be cleaned economically to an ash content of less than 20 percent. Between these extremes lie the bulk of American coals, each having individual cleaning characteristics.

The beneficiation obtainable with respect to sulfur content is similarly variable, though between narrower limits. Sulfur occurring in the form of free, relatively coarse pyrite particles is removed largely by cleaning, but pyrite of microscopic size disseminated in the coal and organic sulfur cannot be removed. An investigation³⁴ of the removal of sulfur from a number of coals by cleaning showed that the percentage reduction in total sulfur content ranged from a few percent with coals high in organic sulfur or finely divided pyrite (an isolated instance showed an actual increase in sulfur) up to 63 percent for coals containing coarser pyrite. Many of the high-sulfur coals contain considerable coarse pyrite and hence are amenable to cleaning.

Only meager data are available on the reduction in phosphorus content obtained in actual washing operations. Laboratory studies³⁵ have shown, however, that the phosphorus present in some coals tends to be associated more with the bony or impure coal than with the clean coal of lower specific gravity. This relationship suggests that phosphorus is generally reduced somewhat by washing. The figures available for three actual washing operations show reductions in phosphorus content of 0, 10, and 38 percent, respectively.³⁶

³⁴ Yancey, H. F., and Parr, S. W., *Ind. Eng. Chem.*, **16**, 501-8 (1924).

³⁵ Davies, R. W., *Fuel*, **5**, 550-7 (1926). Edwards, A. H., and Jones, J. H., *J. Soc. Chem. Ind.*, **55**, 186-9T (1936).

³⁶ Cf. Selvig, W. A., Nicholls, P., Gardner, W. L., and Muntz, W. E., *Carnegie Inst. Tech., Mining Met. Invest., Coop. Bull.* **29** (1926), 61 pp., especially p. 17. Geer, M. R., Davis, F. T., and

Soluble chlorides, when present in coal, are partly dissolved and removed by the water employed in wet cleaning processes. Their removal is governed largely by the amount of coal surface exposed to the solvent action of the water. Thus, Bradley³⁷ has shown that the removal of salt from a South Yorkshire coal ranged from 31 percent in the coal coarser than $\frac{3}{8}$ inch to 63 percent in the 30- to 90-mesh sizes. Reduction of salt content in other English coals ranged from 23 to 75 percent.³⁸

EFFECT OF CLEANING ON UTILIZATION

The attributes of cleaned coal are greater uniformity in composition and, of course, reduced content of impurity. These characteristics, especially uniformity, provide definite advantages in the utilization of coal, for regardless of how coal is used one or more of its impurities are, with few exceptions, deleterious. The injurious effects of impurities have been studied by many investigators.³⁹ Chapman and Mott⁴⁰ have provided a comprehensive discussion of the advantages of clean coal in industrial use.

Actually, the ill effects of the ash-forming impurities in coal are felt even before the coal is used. An economic loss is manifest in the handling, transportation, and storage of high-ash coal, for the inert impurities must be handled with the coal, yet contribute nothing in its use. In combus-

Yancey, H. F., *Am. Inst. Mining Met. Engrs., Tech. Pub.* **1586** (1943), 8 pp.

³⁷ Bradley, G. W. J., *Fuel*, **7**, 31-6 (1928).

³⁸ See p. 21 of Chapman and Mott, ref. 6.

³⁹ Fieldner, A. C., *U. S. Bur. Mines, Rept. Investigations* **3020** (1930), 13 pp., **3114** (1931), 9 pp. Ramsburg, C. J., *Mining Cong. J.*, **16**, No. 2, 68-72 (1930). Mott, R. A., Wheeler, R. V., *Coke for Blast Furnaces*, The Colliery Guardian Co., London, 1930, pp. 142-6. Rice, W. E., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 247-52 (1932).

⁴⁰ See pp. 598-623 of Chapman and Mott, ref. 6.

tion, the ash-forming impurities not only dilute the combustible content of the coal and thus reduce its calorific value but also lower the effective capacity of the burning equipment, reduce plant flexibility, and impose added expense for the handling of ash. Moreover, the fluctuations in ash content that characterize high-ash coals render the control of combustion difficult. That excessive ash content impairs the efficiency of combustion is well known. Hebley,⁴¹ in summarizing comparative burning tests of the same coals before and after cleaning, showed that 1 percent of excess ash in the coal causes a loss in efficiency averaging 0.34 percent.

Another important way in which cleaning affects the combustion characteristics of coal is in its influence on the formation of clinker and slag. The effect of washing coal on the fusibility of its ash is peculiar to each coal, for it depends on the chemical composition of the impurities removed and that of the ash remaining in the washed coal. Selvig and his coworkers⁴² reported the ash-fusion temperature of 12 coals before and after washing; the ash-fusion temperature of 8 increased, 2 remained unchanged, and 2 decreased. Pieces of extraneous impurities, such as shale, were found to serve as nuclei for the formation of large clinkers, and hence the removal of these impurities by cleaning may decrease the formation of clinker even though the ash-fusion temperature of the coal as a whole is not increased. Gould and Brunjes⁴³ determined the ash-softening temperature of several sizes and specific-gravity components of Pennsylvania coals; they pointed out that particles of free impurity frequently are lower in ash-softening tem-

perature than the coal with which they are associated, thus giving favorable conditions for initiating formation of clinker. A similar investigation of Illinois coals, which are generally lower in ash-fusion temperature, showed less variation in the fusion temperature of their components than that found for the Pennsylvania coals.⁴³

The deleterious effects of high ash content in coals used for steam raising have their counterpart in coals converted into coke for metallurgical use. High ash content in the coal decreases the yield of coke in terms of carbon content or thermal value, decreases the yield of byproducts, and gives a weaker coke and consequently more breeze. Use of high-ash coke in blast furnaces causes an increase in the consumption of coke, requires more limestone for flux, reduces furnace capacity, and makes the control of temperature difficult. Various estimates have been made of the increased cost per ton of pig iron attributable to excess ash in the coal used for making metallurgical coke.⁴⁴

Sulfur, second to ash in importance as an impurity, is detrimental in steam coals and domestic fuel largely because of the corrosive action of its products of combustion. It is in metallurgical fuel, however, that sulfur presents its principal disadvantages. Sulfur is a deleterious impurity in virtually all metallurgical products; for this reason, high-sulfur coal is unsuited to smelting or heat-treating processes in which the products of combustion come into direct contact with the material under treatment. In blast-furnace operation, the penalties ex-

⁴³ McCabe, L. C., and Rees, O. W., *Illinois State Geol. Survey, Rept. Investigations* 55 (1939), 31 pp.

⁴⁴ Sweetser, R. H., *Mining and Met.*, 5, 172 (1924). Forrest, L. R., *Proc. Southern Ohio Pig Iron and Coke Assoc.*, October, 1924, pp. 20-32. Kinney, S. P., *Blast Furnace Steel Plant*, 14, 15-24 (1926).

⁴¹ Hebley, H. F., *Trans. Am. Inst. Mining Met. Engrs.*, 130, 79-106 (1938).

⁴² Gould, G. B., and Brunjes, H. L., *Trans. Am. Inst. Mining Met. Engrs.*, 139, 364-83 (1940).

acted by high sulfur content in the coke are added slag volume, increased coke consumption, and greater difficulty of furnace control.⁴⁵ Sulfur in pig iron, derived largely from the coke, requires a longer open-hearth treatment. Phosphorus, like sulfur, is an undesirable impurity in coke used to produce pig iron to be refined by the acid open-hearth or Bessemer processes.

When coals containing more than about 0.05 percent sodium chloride are coked, the refractory lining of the ovens, unless made of silica, suffers from corrosion, often so severe that the lining must be replaced after a few months of use.⁴⁶ Silica bricks are more resistant than fireclay bricks to such attack.⁴⁶

CHEMICAL ASPECTS OF COAL CLEANING

Flotation. Chemical technology is especially applicable to the flotation process of cleaning coal because flotation depends on surface properties and surface phenomena that can be modified or even altered completely by chemical or physicochemical treatment. Such treatment is the aspect of the process with which the material that follows is concerned. The theory and fundamental concepts of flotation are not discussed because they have been developed largely in ore-dressing studies rather than in investigations dealing with coal; moreover, they are discussed adequately in ore-dressing literature.⁴⁷

⁴⁵ Joseph, T. L., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 453-63 (1925).

⁴⁶ Glund, W., and Jacobson, D. L., *International Handbook of the Byproduct Coke Industry*, Chemical Catalog Co., New York, 1932, p. 340.

⁴⁷ Gaudin, A. M., *Flotation*, McGraw-Hill Book Co., New York, 1932, 552 pp.; *Principles of Mineral Dressing*, McGraw-Hill Book Co., New York, 1939, pp. 334-423. Taggart, A. F., del Giudice, G. R. M., and Ziehl, O. A., *Trans. Am. Inst. Mining Met. Engrs.*, **112**, 348-81 (1934). Wark, I. W., *Principles of Flotation*, Melbourne, Australasian Inst. Mining & Met., 1938, 346 pp.

Flotation agents may be grouped according to the purpose for which they are employed. *Frothing agents* are used to promote the formation of a froth, to the bubbles of which air-adherent or unwetted particles become attached and are thus buoyed up to the surface for separation. Frothers are generally slightly soluble organic compounds; small amounts lower the surface tension of water appreciably and thus assist in formation of bubbles. According to Götte⁴⁸ and Gaudin,⁴⁹ they are compounds having heteropolar molecules, the polar part of which has an affinity for water and the nonpolar part an affinity for gas or a repulsion for water. *Collecting agents* are employed to make a water-adherent surface become air adherent, or to increase a natural tendency toward air adherence. Collectors resemble frothers in that they are heteropolar, but, in collectors, the polar part of the molecule must have a special affinity for a specific material, such as coal, while the nonpolar part must have an affinity for gas or a repulsion for water. *Depressing agents* have the opposite action; that is, they promote water adherence or wetting. Like collectors, depressants must be selective in their action, affecting only one of the materials to be separated and not the others. Still other agents are sometimes employed to modify the action of the collector or frother. Particularly with coal, one agent may serve as both frother and collector or have a similar dual capacity.

As Ralston⁵⁰ has pointed out, proximity to coke ovens or gas works frequently has led to the use of coal tars, cresols, and wash waters from scrubbing towers as agents in

⁴⁸ Götte, A., *Glückauf*, **70**, 293-7 (1934).

⁴⁹ Gaudin, A. M., *Principles of Mineral Dressing*, McGraw-Hill Book Co., New York, 1939, p. 368.

⁵⁰ Ralston, O. C., *U. S. Bur. Mines, Rept. Investigations* **3397** (1938), 63 pp.

coal flotation.⁵¹ In fact, Jones and Bury⁵² found that such wash waters not only provided suitable agents for flotation but also caused absorption of their noxious constituents by the coal and thus rendered the water safe for disposal into streams. Petroleum products ranging from naphtha to heavy oil, either alone or in combination with pine oil or cresol, also have been widely employed as frothers.⁵³ Other successful agents are xanthates⁵⁴ or other salts of an organic derivative of sulfothiocarbonic acid; polythionates, particularly those of the multivalent metals;⁵⁵ and mineral oil emulsified with the sodium sulfate salt of oleyl alcohol.⁵⁶ Oxidized oils and waxes of paraffin or naphthene base have been found to function for collection as do fatty acids, and also to serve as frothers.⁵⁷

The contention that flotation agents must have heteropolar molecules was challenged by Luisenko,⁵⁸ who found that mineral salts such as sodium chloride are satisfactory agents. Flotation conducted in a 1 percent sodium chloride solution reduced the ash content of coal to be used in making electrode carbon from 21 to 0.44 percent. In another investigation,⁵⁹ it was

found that paraffin oil employed as an insoluble frother, in combination with cresol as a soluble frother, could be dispensed with wholly or in part if the flotation was conducted in sea water. Interest in the use of mineral salts as agents arises from their low cost and from the observation by Maier, Tzuckermann, and Luisenko⁶⁰ that froths produced with such salts contained less water than those produced with oils; the cost of dewatering the froth is one of the principal obstacles to the use of the flotation process.

Pieters⁶¹ made laboratory tests with a variety of flotation reagents. Both organic acids and alcohol were found to increase in effectiveness with increase in molecular weight. A series of mineral oils tested showed increasing collecting power with decrease in viscosity of oil, probably because the more viscous oils were unable to film the coal particles. Phenol, the most effective agent employed, was strongly affected by changes in pH; the addition of potassium hydroxide, sulfuric acid, ammonia, or other electrolytes decreased its flotation properties.

The S.Y.R.C. flotation process investigated by the Fuel Research Board of Great Britain⁶² is of interest technologically, even though it apparently never progressed beyond the experimental stage. Powdered coal was heated to about 300° C in an inert atmosphere. Oils produced in this heat treatment made the resulting product amenable to flotation without additional agents. It was found that coals which responded readily in ordinary flotation could be cleaned satisfactorily by the S.Y.R.C. process by heating to 300°, but that coals

⁵¹ Van Iterson, F. K. Th., *Chem. Weekblad*, **34**, 633-41 (1937).

⁵² Jones, F. B., and Bury, E., U. S. Pat. 1,388,868 (1921).

⁵³ Pakhalok, I. F., *Ugol*, **1936**, No. 129, 70-6; *Chem. Abs.*, **30**, 8567 (1936). Frantz, P. M., U. S. Pat. 2,028,742 (1936).

⁵⁴ Williams, P. J., Brit. Pat. 272,301 (1926). Kühlwein, F. L., Brit. Pat. 286,456 (1927). Pomin, Ya. N., *Coke and Chem. (U.S.S.R.)*, **4**, No. 2, 56-9 (1934).

⁵⁵ Schaefer, W., Brit. Pat. 289,848 (1927).

⁵⁶ Gillson, J. L., and Mentzer, C. T., U. S. Pat. 2,112,362 (1938).

⁵⁷ Eisele, J., Griessbach, R., and Heuck, C., U. S. Pat. 1,787,938 (1931).

⁵⁸ Luisenko, P. D., *Coke and Chem. (U.S.S.R.)*, **5**, No. 10, 40-6 (1935).

⁵⁹ Minerals Separation Limited, Ger. Pat. 478,065 (1920).

⁶⁰ Maier, L., Tsukerman, L. E., and Luisenko, P. D., *Khim. Tverdogo Topliva*, **5**, 655-61 (1934).

⁶¹ Pieters, H. A. J., *Brennstoff-Chem.*, **12**, 325-7 (1931).

⁶² *Dept. Sci. Ind. Research (Brit.), Fuel Research Board Rept. 1930*, pp. 67-8.

which required strong frothing agents in ordinary flotation necessitated temperatures of about 330° C.

Pyrite is frequently troublesome in the flotation of coal, owing to its tendency to remain unwetted and to float with the coal. Yancey and Taylor⁶³ investigated depressants for coal pyrite; they concluded that the best depressing agents were lime and the oxidation products of pyrite—ferrous and ferric sulfates. Ferric sulfate was a good depressant in the pH range of 4.5 to 6.9 and, under certain conditions, was effective in alkaline circuits. Ferrous sulfate was effective in slightly acid solutions. The depressing action of ferric sulfate was attributed to adsorption by the pyrite of either a ferric hydroxide sol or a basic ferric sulfate slime. Depression was less pronounced in the presence of coal than with pyrite alone, probably because of mechanical entrapment of pyrite particles in the large mass of floating coal particles. Stewart⁶⁴ found that, although lime acted as a depressant for pyrite and marcasite, it also inhibited flotation of the coal. In Stewart's experiments, lime or sulfuric acid was added to the flotation circuit in amounts large enough to vary the pH from 2.0 to 11.2; the greatest reduction in sulfur content occurred at a pH of 10.3 but was accompanied by a reduced yield of coal. Optimum flotation, considering both yield of coal and reduction in sulfur and ash content, occurred with a neutral circuit.

Although clay is wetted by water more readily than coal and pyrite, special treatment sometimes is required to prevent it from floating with the coal. Such agents as sodium carbonate and sodium silicate,

which will disperse or deflocculate clay and shale, have been suggested by several investigators.^{59, 65} When in a dispersed condition the clay particles are wetted more easily. Moreover, dispersion tends to free the coal from clay particles, thus reducing mechanical entrapment and allowing the collector greater access to the coal particles. Potassium ethyl xanthate, in combination with sodium carbonate, was employed by Petersen⁶⁶ to peptize clay so that it could be separated from coal simply by sieving; the same reagents were used by Van Ahlen⁶⁷ for a flotation separation. Yancey and Taylor⁶³ demonstrated that the clay contaminating floated coal was present largely as a suspension in the water entrained in the froth; they concluded, therefore, that the clay content of a froth is influenced principally by the pulp dilution.

A relationship between flotation properties and rank of coal might be expected, owing to differences in the surface properties of the various ranks of coal. Ralston and Wichmann,⁶⁸ as early as 1922, noted a relationship between flotability and rank. Brady and Gauger⁶⁹ have showed that the angle of contact between a bubble of gas and a submerged coal surface ranged from 48° with anthracite, 60° with Pennsylvania bituminous coal, and 57° with Illinois bituminous coal to 0° with North Dakota lignite. Similarly, work of the Fuel Research Board of Great Britain⁷⁰ with vacuum flo-

⁶⁵ Edser, E., and Williams, P. T., *Trans. Fuel Conf., World Power Conf., London, 1928*, 1, 374-84 (1929). Crawford, J. T., *Trans. Am. Inst. Mining Met. Engrs.*, 119, 157 (1936).

⁶⁶ Petersen, W., *Glückauf*, 67, 1445-53 (1931).

⁶⁷ Van Ahlen, A., *Brennstoff-Chem.*, 17, 446-51 (1936).

⁶⁸ Ralston, O. C., and Wichmann, A. P., *Chem. & Met. Eng.*, 26, 500-3 (1922).

⁶⁹ Brady, G. A., and Gauger, A. W., *Ind. Eng. Chem.*, 32, 1599-604 (1940).

⁷⁰ Dept. Sci. Ind. Research (Brit.), *Fuel Research Board Rept.*, 1935, pp. 51-3.

⁶³ Yancey, H. F., and Taylor, J. A., *U. S. Bur. Mines, Rept. Investigations* 3263 (1935), 20 pp. Cf. Yamaguchi, K., *J. Fuel Soc. Japan*, Sec. 2, 7, 126-8 (1928).

⁶⁴ Stewart, J. W., *Mineral Industries (Penna. State Coll.)*, 2, No. 3, 1, 4 (1932).

tation indicated that flotability was at a maximum with coals containing about 92 percent carbon (dry, ash-free basis) and decreased with both decreasing and increasing carbon content. Coals of less than 83 percent carbon were found to be especially difficult to float.

Numerous investigators have suggested flotation as a means of separating the petrographic constituents of coal. Chapman⁷¹ noted that kerosene produced a froth containing 76 percent bright coal (clarain and vitrain) and only 24 percent dull coal or durain compared with phenol, which yielded 20 percent bright coal and 80 percent dull coal. Price⁷² discovered that starch will depress fusain selectively, and Mayer and Schranz⁷³ mentioned the use of organic protective colloids, like starch, glue, tannin, and albumen, to depress dull coal. Methods of selective flotation in which all the coal components except fusain are depressed by the action of polyhexoses pretreated with suitable agents were described by Kühlwein,⁷⁴ Schaefer and Mertens,⁷⁵ and Brownlie.⁷⁶

The "Ekof" method, described by Kühlwein and by Schaefer and Mertens, is conducted in two steps. In the initial step, a fusain concentrate is made by depressing the other components of the coal, polyhexoses treated with hydrochloric acid or other suitable chlorides being the depressing agent. The pulp is then made weakly alkaline, a collecting agent such as a petroleum oil is added, and the remaining

coal is floated away from the refuse. The experimental results obtained by Kühlwein given in Table II indicate the extent to

TABLE II

REDUCTION OF FUSAIN CONTENT BY SELECTIVE FLOTATION⁷⁴

Coal	Fusain Content		
	Un-treated Coal percent	Fusain Concentrate percent	Coal Concentrate percent
Yorkshire	15	35	7
Lower Silesian	9	30	5
Ruhr	11	35	10
Ruhr	15	40	8
Ruhr	16	28	10

which fusain content can be reduced by the Ekof method.

A method of selectively floating fusain developed by Bierbrauer and Pöpperle⁷⁷ depends on differential surface oxidation of the coal components. A small amount of an oxidizing agent (for instance, 250 to 500 grams of potassium permanganate per ton of coal) added to the flotation medium causes oxidation of the humates present in the clarain, vitrain, and durain. The humic acid thus formed as a surface layer is hydrophilic, and consequently these components of the coal are depressed. Fusain, with its lower content of humates, is less affected by the treatment and will float with the aid of a frothing agent. After the fusain has been removed the remainder of the coal is floated away from the refuse by the addition of a stronger collector to overcome the hydrophilic property induced by oxidation. As humate content varies with rank and type of coal, each coal presents an individual problem in the choice of reagents suitable for controlling the process.

⁷⁷ Bierbrauer, E., and Pöpperle, J., *Glückauf*, **70**, 933-40 (1934); Ger. Pats. 619,239 (1935), 650,031 (1937).

⁷¹ Chapman, W. R., *Fuel*, **1**, 52-4 (1922).

⁷² Price, F. G., U. S. Pat. 1,499,872 (1924). See also Edser and Williams, ref. 65.

⁷³ Mayer, E., and Schranz, H., *Flotation*, S. Hirzel, Leipzig, 1931, 450 pp.

⁷⁴ Kühlwein, F. L., *Glückauf*, **70**, 245-52, 275-7 (1934).

⁷⁵ Schaefer, W., and Mertens, W., U. S. Pat. 1,944,529 (1934). *Erz- und Kohle Flotation G.m.b.H.*, Fr. Pat. 743,295 (1933).

⁷⁶ Brownlie, D., *Steam Engr.*, **3**, 5-6, 44 (1933).

EXTRACTION OF ASH-FORMING IMPURITIES BY TREATMENT WITH ACIDS

Removal of the organic components of coal from its inorganic impurities by chemical treatment is now practiced industrially in the hydrogenation and Pott-Broche processes, although elimination of impurities is not the principal objective. The alternative procedure, removal of the inorganic impurities from the organic constituents by treatment with acids, has been employed in the laboratory to produce coal of unusually low ash content suitable for use in making electrodes and special metallurgical coke or as fuel for coal-dust engines. Sustmann and Lehnert⁷⁸ have discussed the field for removal of impurities by acid treatment and reviewed the available literature. These investigators also have reported the results of experiments in which German brown and bituminous coals were treated with various concentrations

⁷⁸ Sustmann, H., and Lehnert, R., *Brennstoff-Chem.*, **18**, 353-6 (1937). See also Selvig, W. A., Ode, W. H., and Gibson, F. H., *U. S. Bur. Mines, Rept. Investigations* **3731** (1943), 22 pp.

of hydrochloric and hydrofluoric acid.⁷⁹ Table III summarizes the reduction in ash content obtained in these tests.

The acid treatment was much more effective with the brown coals than with coals of bituminous rank. According to Fischer, as quoted by Sustmann and Lehnert, this can be attributed in part to the capillary structure of the brown coals, which allows easier penetration of the acid. Much of the ash in brown coal is organically bound, and according to Fischer and Fuchs⁸⁰ that portion of the lime salts present in the form of humates can be removed by mineral acids. In comparing brown and bituminous coals, rank is an important factor, but it would seem that in general the effectiveness of acid treatment should be influenced largely by the chemical nature and physical distribution of the impurities in each particular coal rather than by its

⁷⁹ Sustmann, H., and Lehnert, R., *ibid.*, **18**, 433-8 (1937), **19**, 41-5 (1938). Cf. Pieters, H. A. J., and Smeets, G., *Het Gas*, **53**, 446-8 (1933).

⁸⁰ Fischer, F., and Fuchs, W., *Brennstoff-Chem.*, **8**, 291-3 (1927).

TABLE III

RESULTS OF TREATING COALS WITH HYDROCHLORIC AND HYDROFLUORIC ACIDS⁷⁹

Acid Treatment *	Percentage of Ash, Moisture-Free Basis							
	Brown Coals				Bituminous Coals †			
	A	B	C	D	W	X	Y	Z
Untreated coal	9.9	5.5	11.3	6.7	16.2	1.7	18.4	2.4
0.3 N hydrochloric	3.3	0.8	3.4	1.4	13.8	1.7	18.4	1.9
0.9 N hydrochloric	0.8	0.3	2.1	0.9	12.0	...	18.1	1.9
1.5 N hydrochloric	0.7	0.2	2.1	0.9	11.7	...	18.4	1.9
Hydrochloric followed by dilute hydrofluoric ‡	...	0.06	2.0	0.9	0.4
Dilute hydrofluoric	6.4	...	7.2	0.6

* With brown coals, 100 grams of coal under 4 millimeters in size was boiled for 1 hour in 200 cubic centimeters of acid, concentration being kept constant, and then washed with hot water until water was free of chlorine. With bituminous coals, 500 grams of coal ground to pass a sieve having 100 mesh per square centimeter was boiled with 1,000 cubic centimeters of acid; the remainder of the procedure was the same as with the brown coals.

† Coals W and X were high volatile; coals Y and Z were low volatile.

‡ Fifteen percent hydrofluoric acid for the brown coal, and presumably the same strength for the bituminous coals.

rank. Unfortunately, no information is available on the chemical nature of the impurities in the coals tested.

Dilute hydrofluoric was more effective than hydrochloric acid in removing impurities, and hydrochloric followed by hydrofluoric acid was the most effective treatment found. With the brown coals each gram of hydrochloric acid dissolved about 3 grams of impurities, regardless of the concentration of the acid.

The effect of acid treatment on the ash-fusion temperatures of the coals was observed to vary with the kind and strength of acid employed. Perhaps when the technique of acid treatment becomes more fully developed it will be possible, through choice of suitable reagents and operating conditions, to remove selectively only the impurities that exert a deleterious effect on ash-fusion temperature. In this respect, cleaning by acid treatment offers an advantage over gravity cleaning methods, in which the chemical composition of impurities does not influence their removal except in so far as it determines their specific gravities.

Demann and Schön Müller⁸¹ concluded that treatment with hydrochloric acid was more effective if preceded by treatment with hydrofluoric acid to decompose siliceous impurities. One coal, the initial ash content of which was not given, on treatment with hydrofluoric acid and evaporation to dryness, was reduced in ash content to 3.4 percent by the formation of volatile fluorides. When the fluorides remaining in the coal were leached out with water the ash content was further reduced to 2.6 percent. On final treatment with hydrochloric acid to remove iron compounds the ash was reduced to 0.7 percent. Here, again, no detailed information is available on the

chemical nature of the impurities in the coal. These investigators cautioned against the use of hot acids, for such treatment will attack the constituents responsible for coking properties.

The effectiveness of acid treatment is naturally related to the particle size to which the coal is crushed before treatment. Hankiss⁸² observed that the reduction in ash content possible with coal of 0.5-millimeter size was doubled when the coal was crushed to 0.1 millimeter for treatment.

Fischer and Sustmann⁷⁸ found that a 10 percent solution of formic acid reduced the ash content of a brown coal from 9.6 to 1.6 percent. As pointed out by Sustmann and Lehnert, organic acids are to be preferred to inorganic acids, for if incompletely removed after the treatment they will not produce corrosive fumes during combustion of the coal.

The action of acids on the mineral constituents of coal is the basis of the disintegration process developed by Lessing⁸³ for breaking down coal in mining. Acids attacking the minerals occurring in the cleats and partings of the coal cause it to degrade. Liquid sulfur dioxide under high pressure and to a lesser extent gaseous carbon dioxide have a similar effect.

FLOCCULATION OF COAL SLURRY

The water used in coal-cleaning processes generally must be clarified to make it suitable for reuse or to render it fit for disposal into streams. In Europe, and at a few washeries in the United States, flocculating agents are employed to increase the settling rate of the suspended solids that comprise coal slurry. Figure 6 contrasts the appearance and relative size of coal particles pass-

⁸² Hankiss, S., *Szénkísérleti Közlemények*, **2**, 134-9 (1928); *Chem. Abs.*, **23**, 3557 (1929).

⁸³ Lessing, R., *Colliery Guardian*, **124**, 1211-2 (1922); U. S. Pat. 1,532,826 (1925).

⁸¹ Demann, W., and Schön Müller, J. R., *Glückauf*, **76**, 112-3 (1940).

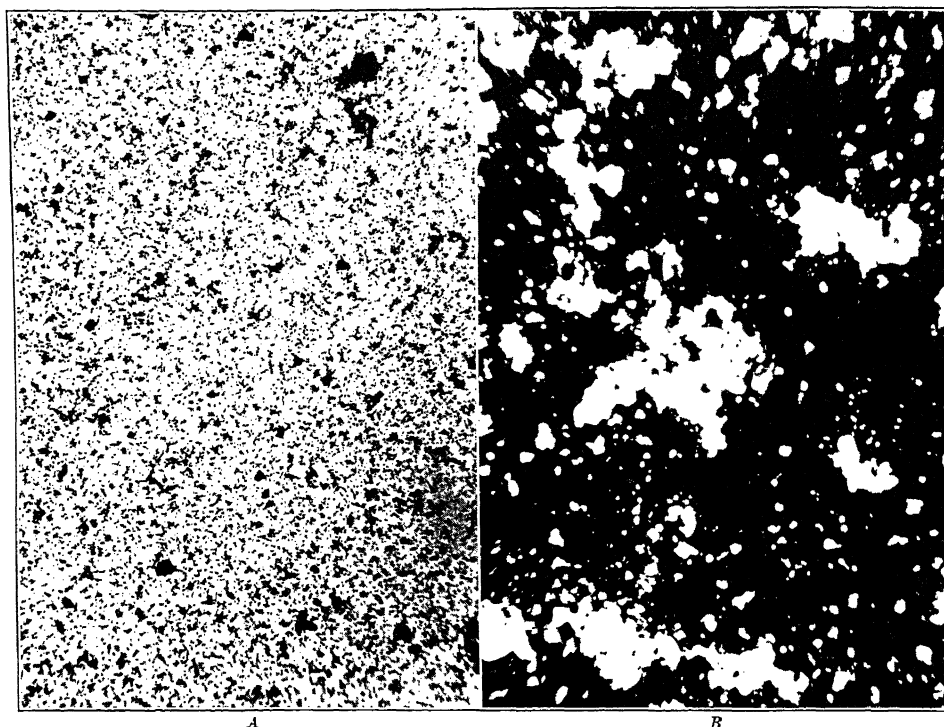


FIG. 6. Particles of coal slurry (A) before and (B) after flocculation with potato starch.

ing 400 mesh (36 microns) before flocculation with the appearance and size of the flocs obtained with potato starch. Starch and lime are the flocculants used industrially, and consequently most of the information available in the literature concerns these materials. However, a wide variety of other materials, both electrolytes and organic colloids, have been used in laboratory experiments. The several theories of the mechanism of flocculation are not described here, for they are discussed adequately in textbooks;⁸⁴ as applied spe-

cifically to coal slurry, the mechanism of flocculation has been described by Lohmann⁸⁵ and Needham,⁸⁶ among others.

Table IV summarizes the results of flocculation tests conducted by Samuel,⁸⁷ Gardner and Ray,⁸⁸ Petersen and Gregor,⁸⁹ and Yancey and coworkers.⁹⁰ These data permit comparison of the effectiveness of the reagents used in each individual investigation but not between investigations, be-

⁸⁶ Needham, L. W., *Trans. Inst. Mining Engrs.*, **92**, 28-58 (1936).

⁸⁷ Samuel, J. O., *Trans. Inst. Chem. Engrs.*, **16**, 47-56 (1938).

⁸⁸ Gardner, G. R., and Ray, K. B., *Trans. Am. Inst. Mining Met. Engrs.*, **139**, 290-309 (1940).

⁸⁹ Petersen, W., and Gregor, F., *Glückauf*, **68**, 621-30 (1932).

⁹⁰ Yancey, H. F., Zane, R. E., Wood, W., and Cannarella, J. T. H., *U. S. Bur. Mines, Rept. Investigations* **3494** (1940), 13 pp.

⁸⁴ Freundlich, H., *Colloid and Capillary Chemistry* (translated from the 3rd German ed. by H. S. Hatfield), Methuen & Co., London, 1926, 883 pp. Kruyt, H. R., *Colloids*, 2nd ed. (translated by H. S. van Klooster), John Wiley & Sons, New York, 1930, 286 pp.

⁸⁵ Lohmann, G., *Glückauf*, **72**, 1121-33 (1936).

TABLE IV

RELATIVE EFFECTIVENESS OF VARIOUS FLOCCULATING AGENTS, AS REPORTED BY DIFFERENT INVESTIGATORS

Samuel ⁸⁷		Gardner and Ray ⁸⁸		Petersen and Gregor ⁸⁹		Yancey, Zane, Wood, and Cannarella ⁹⁰	
Reagent *	Time for Suspension to Clear minutes	Reagent †	Settling Index seconds per centimeter	Reagent ‡	Height of Column of Clarified Water after 4 Minutes of Settling millimeters	Reagent §	Solids in Suspension after 10 Minutes of Settling percent
Ca(OH) ₂	3.5	No reagent	65	No reagent	21	No reagent	3.83
CaCl ₂	23.0	Starch A	6	FeCl ₃	23	Mogul	0.07
CaSO ₄	29.0	Crude potato starch	5	Ca(OH) ₂	24	Wheat flour	0.12
Ca(NO ₃) ₂	51.0	Refined potato starch	5	Na ₃ PO ₄	25	Potato starch	0.10
Ba(OH) ₂	7.0	Soybean flour	6	ZnSO ₄ ·7H ₂ O	28	Konjaku	0.10
BaCl ₂	33.0	Soybean meal	7	NaOH	39	Cornmeal	0.32
Ba(NO ₃) ₂	67.0	Wheat bran	6			Unifloc	0.24
KOH	10.5	Distillery waste	8	Soap	32	Mogul and NaOH	0.07
NaOH	10.0	Crude cornstarch	6	Gum arabic	54	Wheat flour and NaOH	0.11
NaCl	93.0	Gluten	6	Gelatin	64	Potato starch and NaOH	0.04
Na ₂ SO ₄	110.0	Zein	11	Potato starch	81	Konjaku and NaOH	0.09
NaNO ₃	195.0	Pearl starch C	6	Carraghen moss	100	Cornmeal and NaOH	0.13
LiOH	4.0	Starch B	7	Linseed extract	107	Mogul and alum	0.09
NH ₄ OH	23.0	Powdered starch D	6	Oil emulsion	122	Wheat flour and alum	0.09
(NH ₄) ₂ SO ₄	129.0	Beef extract	8			Potato starch and alum	0.08
NH ₄ Cl	120.0	Tapioca flour	6			Konjaku and alum	0.05
NH ₄ NO ₃	150.0	Oak sawdust	14			Cornmeal and alum	0.13
		Wheat straw	16			Mogul and FeCl ₃	0.11
						Wheat flour and FeCl ₃	0.09
						Potato starch and FeCl ₃	0.05
						Konjaku and FeCl ₃	2.10
						Cornmeal and FeCl ₃	0.08
						NaOH	2.46
						Alum	2.17
							0.66

* Concentration of reagent in slurry, 0.02 percent.

† Concentration of reagent in slurry, 0.5 pound of causticized starch per ton of solids; solids, 5 percent.

‡ Concentration of electrolyte in slurry, 0.05 percent; of colloid, 0.01 percent; solids, 4 percent.

§ Concentration of reagent in slurry, 0.001 percent, mixtures composed of equal amounts of components; solids, 5 percent.

|| Sample taken at midpoint of column of supernatant layer.

cause of the variation in the methods of reporting results and differences in the coals used. Among the electrolytes examined by Samuel, the hydroxides were decidedly the most effective flocculants, while the nitrates showed the least clarifying action. With Samuel's data, as with those of the other investigators, all reagents are compared at the same concentration; actually each reagent has an optimum concentration for maximum effectiveness, and consequently

the figures in the table do not necessarily show the best flocculation obtainable with each reagent.

All the amylaceous materials tested by Gardner and Ray appear to be about equally effective, as measured by the rate at which the solid meniscus falls during clarification. A rate of fall of 5 seconds or less per centimeter is considered good, and 6 to 10 seconds is fair clarification. The concentration of electrolytes used by

Petersen and Gregor was five times that of the colloidal reagents they employed; most other investigators also have observed that the concentration of reagent required for effective clarification is greater with electrolytes than with colloids. As shown by the data of Yancey and coworkers for ordinary slurries, mixtures of reagents consisting of both electrolyte and colloid offer some advantages over colloids used alone.

Both Petersen⁹¹ and Yancey and coworkers stated that qualitatively the amount of reagent required for flocculation is influenced by the rank of the coal, consumption of reagents increasing with decrease in rank; probably this relationship can be attributed to differences in surface properties.

Of greater importance are the nature and quantity of the impurities in the slurry. Table V shows that coal and its principal

impurities, bone and shale, behave quite differently in flocculation. With shale starchy reagents, although satisfactory with both coal and bone, are not as effective as some of the electrolytes. A colloidal reagent superior to starches in treating shaly slurry is konjaku, prepared from a tuber (*Hydrosme rivieri*) grown in Japan.⁹² Slurries containing up to 20 percent shale are flocculated readily with konjaku, but slurries containing more shale are stabilized.⁹⁰ Raybould⁹³ stated that because clay adsorbs lime the amount of that reagent required for flocculation depends on the clay content of the slurry. However, this action tends to retard disintegration of the clay and in that respect is beneficial. Hard water also retards the disintegration of shale and clay.⁹⁴

Wilkins⁹⁵ found that the amount of starch or gelatin required to flocculate some slurries that were difficult to clarify could be reduced if the slurry was "sensitized" by the addition of wetting agents or other surface-active substances. Effective sensitizers were turkey-red oil, phenol, cresols, castile soap, and certain wetting agents. If used in excess, however, the sensitizers reduced the settling rate.

Although Gardner and Ray⁸⁸ found but little difference in the effectiveness of various starches, they did find that the temperature at which the potato starch was prepared influenced its flocculating properties. Flocculating power increased with increase in temperature of preparation in the range from the temperature of the gelatinization point up to 145° C; above this tem-

TABLE V

FLOCCULATION PRODUCED BY COLLOIDS AND ELECTROLYTES ON SLURRIES OF BITUMINOUS COAL AND ITS COMMON IMPURITIES⁹⁰

Reagent	Percent Reagent Added	Percent Solids Remaining in Suspension after 10 Minutes of Settling *		
		Coal	Bone	Shale
None	1.48	1.21	2.44
Colloids				
Mogul	0.0025	0.07	0.03	0.64
Wheat flour	0.0025	0.08	0.08	1.13
Potato starch	0.0025	0.24	0.10	2.34
Unifloc	0.0050	0.07	0.08	0.42
Electrolytes				
Lime	0.01	0.84	0.40	0.11
Ferric chloride	0.01	0.08	0.06	0.24
Ferric chloride	0.02	1.14	0.06	0.08
Hydrochloric acid	0.01	0.09	0.09	0.05
Hydrochloric acid	0.02	0.12	0.08	0.04
Alum	0.01	0.06	0.23	2.18
Alum	0.02	0.05	0.07	0.24
Aluminum sulfate	0.01	0.07	0.23	2.70
Aluminum sulfate	0.02	0.08	0.07	0.10
Sodium hydroxide	0.01	1.82	1.70	2.91
Sodium hydroxide	0.02	1.71	1.16	2.72

* Five percent initial solids, through 325 mesh.

⁹¹ Petersen, W., *Glückauf*, **70**, 125-31 (1934).

⁹² Van Iterson, F. K. Th., *Proc. Acad. Sci. Amsterdam*, **41**, 81-94 (1938).

⁹³ Raybould, W. E., *Trans. Inst. Mining Engrs.*, **SS**, 194-229 (1935).

⁹⁴ Lomax, W., and Statham, I. C. F., *Colliery Eng.*, **16**, 124-7, 137, 164-8, 225-31 (1939).

⁹⁵ Wilkins, E. T., *J. Soc. Chem. Ind.*, **54**, 391-3T (1935).

perature it decreased. The increased effectiveness, especially that obtained above 100° C, was ascribed to hydrolysis of the amylopectin, the phosphoric acid ester of the starch, to form soluble amylose and phosphoric acid.

Many investigators have pointed out that ordinary starch solutions lose their effectiveness on standing, probably because of bacterial fermentation. Gardner and Ray found that pressure heating of the starch tended to preserve its flocculating power. The addition of an electrolyte like sodium hydroxide is also effective.⁹⁶ In the patented Henry⁹⁷ process the starch granules are first burst open by freezing at -6° C, and the frozen starch is then acted upon by a hot dilute solution of sodium hydroxide. This preparation is added to the slurry, which has previously been made alkaline with lime. Typical concentrations of the three reagents in the slurry are: lime, 0.03; starch, 0.0007; and caustic soda, 0.002 percent. One ounce of the prepared starch is reported to be sufficient to treat 1,000 gallons of slurry. The Henry process is used in various European plants, but neither van Iterson⁹² nor Petersen⁹¹ could find any advantage in the use of frozen starch.

Another patented flocculating agent widely used in England is Unifloc, developed by Samuel.⁹⁸ This material is a gel, easily dispersible in water, which consists of starch, calcium chloride, and zinc chloride. To produce the gel, 10 grams of potato starch in 20 cubic centimeters of water is added with constant stirring to a hot solution consisting of 5 grams of anhydrous calcium chloride and 3 grams of anhydrous

zinc chloride in 20 cubic centimeters of water; the whole is then vigorously stirred at a temperature of 70 to 150° C, the complete treatment consuming 15 to 20 minutes. According to Samuel, zinc chloride aids gelification and produces a gel that gives larger and heavier flocs than those obtained when only calcium chloride is used with starch. The gel is elastic and permanently stable with respect to its flocculating power, and it disperses in water to form a hydrophilic colloid having a strong positive charge. As with the Henry process, Unifloc works best when added to an alkaline slurry, although Samuel claimed that it would flocculate any slurry having a pH of 3 to 12.

Other specially prepared amylaceous materials which have been successful for flocculating coal-washery water are Mogul, which has been used in this country, Ogwen powder and B-4, in England, and Flocgel, which has been used in the Netherlands and is also made in the United States.⁹²

At the flocculation plant of a coal washery in Yorkshire,⁹⁹ lime was added to a portion of the circulating water at the rate of 1 pound for each 100 gallons of slurry per hour. The consumption of lime was estimated to be as follows: aeration (carbon dioxide, etc.), 20; softening action on water, 10; alkalinity of filtered water, 20; adsorption by solids, 30; and excess and loss, 20 percent.

Oil emulsions are good clarifying agents if properly dispersed. Petersen and Gregor⁹⁹ have described experiments in which flocculating agents were prepared from various distillation products of tar such as crude benzol, tar oil, raw cresol, and anthracene oil by emulsification in water with the aid of a technical soap or a sodium alkyl sulfonate as a wetting agent. Under

⁹⁶ Campbell, C. Q. McW., U. S. Pats. 1,942,507 (1934), 2,051,983 (1936).

⁹⁷ Henry, R. A., Brit. Pat. 322,798 (1928). Berthelot, C., *Usine*, 46, No. 25, 37 (1937).

⁹⁸ Samuel, J. O., and Emlyn Anthracite Colliery Ltd., Brit. Pat. 435,126 (1935).

⁹⁹ Anon., *Colliery Eng.*, 13, 45-52 (1936).

the action of the wetting agent the oils were dispersed to such an extent that they acted as hydrophilic colloids. Although these emulsions carried negative charges, they flocculated coal slurry in a way similar to the action of protective colloids.

DUSTPROOFING COAL

A step in coal preparation in which chemical technology plays an important role is the treatment of coal to render it dustless. Nondrying agents, like petroleum oil, oil emulsions, wax, petrolatum, or solutions of hygroscopic salts, are sprayed onto the coal to agglomerate fine, dust-size particles and fix them to the larger pieces of coal by surface tension.

Experiments by Fife and Edeburn¹⁰⁰ in which the amount of wax contained in various size fractions of a wax-treated coal was determined by extraction of the wax with ethylene dichloride demonstrated that the quantity of dustproofing agent required for satisfactory treatment was a function of the surface area exposed by the coal. Coal 1 to $\frac{3}{4}$ inch in size was found to require only 0.5 pound of wax per ton in comparison with 280 pounds per ton for the coal finer than 200 mesh—such is the rapid increase in specific surface as particle size decreases. Similarly, Pilcher and Sherman¹⁰¹ reported that the quantity of oil required to dustproof different sizes of the same coal ranged from 0.3 quart per ton for the $\frac{3}{8}$ -inch to $1\frac{1}{2}$ -inch size to 8.2 quarts per ton for the coal finer than $\frac{3}{8}$ -inch.

A relationship between type of dustproofing agent and rank of coal is shown by the work of Pilcher and Sherman and

that of British investigators.¹⁰² Oils of low viscosity, say 100 seconds (Saybolt Universal) at 100° F, and solutions of calcium chloride were found to be effective for coals of high rank but less satisfactory for lower-rank coals, such as that from the Illinois No. 6 bed. However, oils of 600 seconds viscosity and blends of oil and petrolatum or asphalt proved more suitable than light oils for low-rank coals and had about equal effectiveness with coals of all ranks. Failure of the lighter oils and of calcium chloride solutions to dustproof coals of lower rank satisfactorily was attributed to the greater porosity of such coals and absorption of the dustproofing agent into pores and cracks. The materials of higher viscosity could not be absorbed into the minute pores and hence were equally effective with both porous and nonporous coals. Blocking of the pores and cracks to prevent penetration of the dustproofing fluid is being attempted by the Fuel Research Board; experiments using a mineral oil containing 1 to 2 percent raw rubber or a proprietary substance of molecular weight 50,000 to 100,000 (understood to be an isobutylene polymer) have shown promise.

Numerous secondary advantages, in addition to its primary attribute of dustlessness, have been ascribed to dustproofed coal; most of these lack experimental confirmation. Pilcher and Sherman found that the treatment of coal with oil reduced the retention of extraneous water and mitigated the problem of freezing in shipment. In burning tests on a residential-type underfeed stoker, however, they could find no appreciable effect on performance attributable to treatment with oil in the amounts required for dustproofing. Ambrose and Gaspari¹⁰³ have shown that when coal was

¹⁰⁰ Fife, H. H., and Edeburn, F. W., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 143-55 (1938).

¹⁰¹ Pilcher, J. M., and Sherman, R. A., *Bituminous Coal Research Inc., Tech. Report 6* (1939), 36 pp.

¹⁰² Dept. Sci. Ind. Research (Brit.), *Fuel Research Board Rept.* (1938), pp. 89-96.

¹⁰³ Ambrose, H. A., and Gaspari, H. J. R., *Coal Age*, **42**, 252-4 (1937).

treated with a sufficiently nonviscous oil the clogging of the pores and filming of the surfaces that resulted reduced the oxidation rate of the coal and hence decreased its tendency toward spontaneous heating. Only with the coarser sizes of coal, however, was the amount of oil necessary to obtain this effect within the limit economi-

cally feasible in dustproofing. The finer sizes of coal, those less than 8 or 10 mesh, offered so much surface that the amount of oil required was excessive.

A review of the literature on dustproofing was made by Schmidt¹⁰⁴ in 1937.

¹⁰⁴ Schmidt, L. D., *U. S. Bur. Mines, Circ. 6932* (1937), 10 pp.

CHAPTER 17

CONDITION OF WATER IN COALS

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The nature of the source material from which coal is formed, the coalification process, subsequent experiences of this material on its way from seam to market, as well as the many transformations through which it may go in utilization, all combine in making water an important component of coals from both the scientific and the practical point of view. Coal is formed from vegetation that has accumulated and decayed in swamps. Vegetation itself has a high percentage of water which is to some extent both physically and chemically bound. The water percentage is increased in the process of peat formation in the swamp. The swamp presents us with a mechanical mixture of vegetation, water, and minerals.

During the coalification process when the swamp vegetation is changed first to peat and later to coal, varying amounts of water are present at different stages. In general, the progress of this process is marked by continual elimination of water, particularly in the later stages. This is apparent from a comparison of the moisture contents of the different ranks of coal from lignite to anthracite.

Many coals are washed with water during preparation for market; water is present in most mines and circulates through many coal seams; and frequently coal is subject to natural rainfall in transport or

in storage. Occasionally, firemen add water to coal prior to firing.

Thus it is seen that water plays an important role during the entire course of the gigantic chemical process from carbon dioxide through plants, peat, lignite, the various ranks of coal, and back to carbon dioxide. From the practical as well as the scientific angle it is important to know something of the condition of water in coal.

QUANTITATIVE DETERMINATION OF WATER IN COAL

That the quantitative determination of water in coals of various ranks presents a problem of great difficulty is attested by the many scientists who have studied the problem and the many methods that have been proposed for the determination. Three factors involved in the problem are of paramount significance. One is the desire for a rapid, simple method; the second is the lack of a satisfactory definition of the water in coal; and the third is the difficulty of obtaining a satisfactory sample for moisture determination. Were all the moisture in coal present as free water possessing a normal vapor pressure, it would be a relatively simple matter to drive it off at a temperature slightly above the boiling point, absorb it in a suitable absorbent, and weigh it. According to Terres

and Kronacher,¹ Richardson, working under Liebig's direction, in 1838 brought up the question of hygroscopic or chemically bound water, and concluded from experiments involving weight losses at 100 and 185° C that there were chemical compounds of water in coal. Moreover, the very careful work of Mack and Hulett and of Hulett, Mack, and Smythe² demonstrated that drying at 105° C for 1 hour was insufficient to remove all the water originally present as such, but that additional water was given off continuously as the temperature of drying was increased. Water of decomposition was not given off by the coals that they tested until a temperature of at least 275° C was reached. By their method of direct determination, upwards of 30 percent more water was obtained than by the normal standard method.

According to Somermeier,³ lignitic coals give up their moisture more slowly than harder coals. Barrett, Foott, and Reilly⁴ showed that water given off at 200° C in atmospheres of carbon dioxide, carbon monoxide, hydrogen, and nitrogen for seven days was in each gas slightly in excess of moisture as determined at 105°.

In general, it is customary to consider the water content of coals as being that water which exists as H₂O and can be driven off at 105° C or, at most, at the boiling point of xylene. This leaves out of consideration the water held very tenaciously as such, as well as the water of decomposition.

Both direct and indirect methods have been proposed for the determination of

the water as defined in the preceding paragraph, the indirect being the more prominent.

INDIRECT METHODS

All the earliest attempts at coal analysis involved determination of loss in weight in a drying oven. Thus¹ Kerl in his *Probierbuch* was satisfied with drying a weighed sample in an air bath at 120–150° C, cooling in a desiccator, and weighing, while Muck kept the sample 2 hours between two watch glasses, yet said for accurate results one must work in an air bath joined to an air pump. Hinrichs⁵ believed that the moisture content of finely pulverized coal could be determined by loss in weight when kept at 115° C for 1 hour. According to him, large particles gave unreliable results and a time limit was necessary because original loss in weight was followed by a gain in weight attributed to oxidation. Thus it was early recognized in coal research that the problem of moisture determination in coals was complicated by other factors such as absorption of gases or loss of substances other than water during the drying process. Many investigators⁶ have noted that carbon dioxide, methane, and nitrogen may be given off in measurable quantities at the temperature of boiling water.

Grave concern was felt both in this country and abroad with the existing technique for analysis of coals during the first decade of this century. It was evident that a real

⁵ Hinrichs, G., *Z. anal. Chem.*, **8**, 132–4 (1869).

⁶ Richters, E., *Dinglers Polytech. J.*, **190**, 398–401 (1868), **195**, 315–31, 449–58 (1870), **196**, 317–35 (1870). Von Meyer, E., *J. prakt. Chem.*, **5**, 144–83, 407–27 (1872). Parr, S. W., and Barker, P., *Univ. Illinois, Bull.* **32** (1909), 28 pp. Kropf, H. L., *Het Gas*, **38**, 233–4 (1918). Monro, A. D., *J. Soc. Chem. Ind.*, **41**, 129–32T (1922). Schoorl, N., *Chem. Weekblad*, **21**, 393–5 (1924). Thom, W. T., *Colliery Guardian*, **130**, 558–9 (1925).

¹ Terres, E., and Kronacher, H. K., *Gas- u. Wasserfach*, **73**, 645–51 (1930).

² Mack, E., and Hulett, G. A., *Am. J. Sci.*, **43**, 89–110 (1917). Hulett, G. A., Mack, E., and Smythe, C. P., *ibid.*, **45**, 174–84 (1918).

³ Somermeier, E. E., *J. Am. Chem. Soc.*, **28**, 1630–8 (1906).

⁴ Barrett, W. J., Foott, C. H., and Reilly, J., *J. Soc. Chem. Ind.*, **47**, 142–3T (1928).

need for standardization existed. Studies were conducted by a joint committee of the American Society for Testing Materials and the American Chemical Society as well as by an international committee on analysis. The work of the American committee resulted in a standard method for determination of water which is essentially the same as the present A.S.T.M. standard method.⁷ The international committee recommendations⁸ are in substantial agreement with the conclusions of the joint committee of the American Society for Testing Materials and the American Chemical Society. Fieldner and his associates have reviewed the work since 1899 of different committees appointed to study and devise methods of testing coal and coke.⁹

Other indirect methods have been proposed from time to time. Some of these have no advantages and some disadvantages over the standard method. Thus drying over sulfuric acid or other drying agent in a desiccator is time consuming and does not always remove as much water as the standard method.¹⁰ The results obtained by the use of the Ihlow apparatus and drying to constant weight at the boiling point of xylene in a vacuum do not always agree among themselves.¹¹

⁷ Noyes, W. A., *J. Ind. Eng. Chem.*, **5**, 517-28 (1913). Stanton, F. M., and Fieldner, A. C., *U. S. Bur. Mines, Tech. Paper S* (1913), 42 pp. Fieldner, A. C., *U. S. Bur. Mines, Tech. Paper 76* (1914), 58 pp. *Am. Soc. Testing Materials, Standards 1939*, Pt. III, 15-22.

⁸ Holloway, G. T., and Coste, N., *Rept. Intern. Com. on Anal., 8th Intern. Congr. Applied Chem.*, **1912**, 77-135. Lessing, R., *Orig. Communications, 8th Intern. Congr. Applied Chem.*, Appendix Sections I to V, **25**, 41-90 (1912).

⁹ Calkins, W. B., Fieldner, A. C., Fulweiler, W. H., Selvig, W. A., *Intern. Congr. Testing Materials 1927*, II, 641-5.

¹⁰ Huntly, G. N., and Coste, J., *J. Soc. Chem. Ind.*, **32**, 62-7 (1913).

¹¹ Ihlow, F., *Chem.-Ztg.*, **47**, 185-6 (1923). Blacher, C., and Girgensohn, G., *ibid.*, **48**, 357-71 (1924). Vondracek, R., and Mosendz, L., *Brennstoff-Chem.*, **12**, 445-6 (1931).

The use of the dielectric constant as a function of the moisture content has been proposed for determining the percentage of water in brown coals and other materials.¹² Bielenberg and Zdralek concluded that the dielectric-constant increase with increasing water content does not follow the law of mixtures. The dielectric constant is dependent not only on the moisture content but on the structure of the coal as well. This should be anticipated, since part of the water is bound to the coal surface by forces which are probably electronic in nature. In consequence, the method requires frequent careful calibration. It has found favor in the brown-coal industry for continuous recording of the moisture in coal fed to the briquetting plant.¹³ The technique is unquestionably applicable for this purpose since the coal substance is constant and the variable is the moisture content.

Dolch¹⁴ proposed a "cryohydrate" method as follows: 9 grams of a high-moisture, or 20 grams of a bituminous, coal is placed in an Erlenmeyer flask, and 100 cubic centimeters absolute alcohol is

¹² Ebert, L., *Angew. Chem.*, **47**, 305-15 (1934). Argue, G. H., and Maass, O., *Can. J. Research*, **13B**, 156-66 (1935). Van Steenberg, B., *Het Gas*, **55**, 137-9 (1935). Kotkov, S. A., *Zavodskaya Lab.*, **5**, 358-9 (1936). Arnold, E. A., *J. Inst. Fuel*, **10**, 418-9 (1937). Knoke, S., *Z. Elektrochem.*, **43**, 749-51 (1937). Bielenberg, W., and Zdralek, O., *Braunkohle*, **38**, 699-702 (1939).

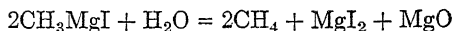
¹³ Erimescu, P., *Braunkohle*, **31**, 868-70 (1932). Velten, O., *ibid.*, **36**, 565-9 (1937). Schultz, F., *ibid.*, **38**, 393-7, 415-19 (1939).

¹⁴ Dolch, M., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 425-47 (1928). Dolch, M., and Strube, E., *überschles. berg- und hüttenmänn. Ver. Katowice*, **68**, 349-52 (1929). Dolch, M., Pöschmüller, E., and David, M., *Chem. App.*, **16**, 137, 151 (1929). *Braunkohle*, **28**, 429-34 (1929). Dolch, M., *Brennstoff-Chem.*, **11**, 429-32 (1930). Dolch, M., *Montan. Rundschau*, **23**, 193-8 (1931). *Brennstofftechnisches Praktikum*, Wilhelm Knapp, Halle, 1931, 148 pp. Thau, A., *Gas World*, **92**, No. 2378, Coking Sect. 10 (1930). Mikulina, N. V., Karelin, A. I., and Shakhno, A. P., *Coke and Chem. (U.S.S.R.)*, **4**, 60-4 (1934).

added. The mixture is boiled for 2 minutes and then cooled and filtered through a folded filter. The first filtrate is discarded, and then a sample of 25 cubic centimeters is mixed with 25 cubic centimeters of petroleum oil. This mixture is warmed until clear and then cooled with rapid stirring to the cloud point. The temperature of the cloud point is a function of the water content which is read from a calibration chart. A determination can be made in 10 minutes. Dolch claimed that the method removed adsorbed water also and that the results were higher than with other methods.

Methods have also been proposed which depend upon measuring the dilution of a reagent when used to treat the coal.¹⁵ Thus Fischbeck and Einecke proposed to determine water content by treating a weighed sample with cold glacial acetic acid and determining the water from measurement of the conductivity of the liquid. Greenfield and Dummett suggested treating with standard acid and determining the dilution by titration with standard alkali solution. Both these methods are open to objection if soluble minerals such as calcium carbonate are present, although Greenfield and Dummett suggested a procedure to correct for soluble minerals. However, this "is only carried out when the tester has reason to believe from his general knowledge and experience that the result given by the original titration is high."

Taubmann¹⁶ has applied the method of Zerewitinoff which involves the measurement of methane formed by the following reaction:



The method is cumbersome and expensive since water-free pyridine and pure magnesium methyl iodide are required. A similar gasometric method suggested first by Dupre¹⁷ for other materials depends upon the reaction between calcium carbide and moisture with measurement of the acetylene formed. Indirect methods of this type have found little favor.

Other miscellaneous indirect methods depend upon the measurement of density of alcohol after leaching sample with water-free reagent,¹⁸ change in conductivity of coal with varying moisture,¹⁹ measurement of refractive index of reagent used for leaching the coal,²⁰ and measurement of vapor pressure of water over the sample.²¹ These are all subject to errors due to the nature of the sample.

DIRECT METHODS

The need for a direct method of determining water in coals has been generally recognized for a long time.²² In 1912, Hil-

¹⁷ Dupre, P. V., *Analyst*, **31**, 213-7 (1906). Piatschek, H., *Braunkohle*, **27**, 49-53 (1928). Von Walther, R., and Benthin, G., *Braunkohlenarch.*, No. **23**, 110-22 (1929). Ruff, O., Friederich, C., and Ascher, E., *Z. angew. Chem.*, **43**, 1083 (1930). Braunschweigische Kohlenbergwerke and Helmut Piatschek, Ger. Pat. 640,346 (1936). Naklonov, V. A., *Zavodskaya Lab.*, **6**, 187-8 (1937).

¹⁸ Mannheimer, M., *Ind. Eng. Chem., Anal. Ed.*, **1**, 154-6 (1929).

¹⁹ Tübben, L., *Braunkohle*, **25**, 200-1 (1926-7).
²⁰ Von Walther, R., and Bielenberg, W., *Braunkohlenarch.*, No. **25**, 17-26 (1929).

²¹ Swietoslawski, W., Brzustowska, H., and Krakowski, M., *Roczniki Chem.*, **14**, 633-9 (1934); *Ann. acad. sci. tech. Varsovie*, **1**, 115 (1935); *Fuel*, **14**, 305-6 (1935).

²² Varrentrapp, F., *Dinglers Polytech. J.*, **175**, 156-8 (1855), **178**, 379-83 (1855). Lord, N. W., *U. S. Geol. Survey, Bull.* **323** (1907), 49 pp.; *U. S. Bur. Mines, Bull.* **28** (1911), 51 pp. Dennstedt, M., and Bünz, R., *Z. angew. Chem.*, **21**, 1825-35 (1908). Porter, H. C., and Ovitz, F. K., *J. Am. Chem. Soc.*, **30**, 1486-507 (1908). Cris-

¹⁵ Fischbeck, K., and Einecke, E., *Z. Elektrochem.*, **35**, 765-9 (1929). Stanworth, S., *Trans. Am. Ceram. Soc.*, **32**, 443 (1933). Greenfield, G. J., and Dummett, G. A., *Fuel*, **16**, 183-8 (1937).

¹⁶ Zerewitinoff, T., *Z. anal. Chem.*, **50**, 680-91 (1911). Taubmann, A., *ibid.*, **74**, 161-7 (1928).

lebrand and Badger pointed out that

methods for determining, in general, belong to the class of indirect methods, which in the absence of a simple reagent for water are most convenient and expeditious; but when applied to so complex and easily oxidized a substance as coal, a number of reactions occur which greatly modify the results. In general these reactions are:

(a) The sensitiveness of coal to atmospheric conditions, especially when finely powdered.

(b) The giving off of volatile substances other than water.

(c) The absorption of oxygen which may take the form of:

1. Oxygen added directly to the coal substance.
2. Oxygen combined with carbon and split off as carbon dioxide.
3. Oxygen combined with hydrogen and split off as water.

field, J. A. P., *J. Franklin Inst.*, **172**, 495-502 (1911). Archibald, E. H., and Lawrence, J. N., *J. Ind. Eng. Chem.*, **4**, 258-62 (1912). Hillebrand, W. F., and Badger, W. L., *Proc. 8th Intern. Congr. Applied Chem.*, **10**, 187-94 (1912). White, J., *J. Franklin Inst.*, **173**, 201 (1912). Winmill, T. F., and Graham, J. I., *J. Soc. Chem. Ind.*, **33**, 1000 (1914). Hinrichsen, F. W., and Taczak, S., *Die Chemie der Kohle*, W. Engelmann, Leipzig, 1916, p. 313. Boddart, R. J., *Het Gas*, **42**, 121-4 (1922). Rutten, J., *ibid.*, **42**, 59-63 (1922). Lunn, C. A., and Knobloch, G. H., *Am. Gas Assoc. Monthly*, **4**, 571-6 (1922). *Dept. Sci. Ind. Research (Brit.) Fuel Research, Phys. Chem. Survey Natl. Coal Resources*, **2** (1923), 28 pp. Kreulen, D. J. W., *Fuel*, **5**, 345-6 (1926). Norlin, E., *Intern. Congr. Testing Materials*, **II**, 674-83 (1927). Dolch, M., and Reinhardt, K., *Braunkohle*, **28**, 709-16, 736-41, 753-9 (1929). Somija, T., and Hirano, S., *J. Soc. Chem. Ind. Japan*, **32**, Suppl. Binding 247-8 (1929). Koelsch, H., *Gas- u. Wasserfach*, **73**, 1047-50 (1930). Šimek, B. G., Ludmila, J., and Stancelova, B., *Mitt. Kohlenforschungs Inst. Prag*, **1**, No. 4, 242-53 (1932). Rzymowska, C., *Przemysł Chem.*, **16**, 265-7 (1932). Midland Coke Research Committee, Report of Progress during 1932, Anon., *Gas World*, **99**, No. 2552, Coking Sect. 73-5 (1933); *Gas J.*, **202**, 916 (1933). Karmaus, H. J., *Emailwaren-Ind.*, **10**, 144-5 (1933). Merlin, A., *14th Congr. chim. ind., Paris*, October, 1934, 8 pp. Stadnikoff, G. L., *Khim. Tverdogo Topliva*, **5**, 193-200 (1934). Kaiser, M., and Spallek, F., *Braunkohle*, **38**, 65-70, 84-91 (1939).

These authors also pointed out the influence of atmospheric humidity on air-drying losses. To these complicating factors must be added the fact that all the water in many coals is not given off until temperatures upwards of 275° C are reached,² and that gases may be absorbed by many coals.

The earliest experiments seeking a direct determination of moisture in coal depended on driving the water off in a current of heated air or other gas, absorbing it in a drying tube, and noting the gain in weight.²³ In general the method is considered too cumbersome for technical use. If air is used, oxidation may result in formation of carbon dioxide and water as has already been noted.

Schläpfer,²⁴ applying the principle of distillation with a liquid immiscible with water (cf. Graefe who used "solar oil"²⁵ and Hofmann-Marcusson who used distillation with xylene for determination of water in tars, etc.²⁶), published in 1914 the results of a very careful study of the determination of water in coal by distilling the sample with xylene. He pointed out the chief sources of error, namely, faulty calibration of the buret in which the volume of water is read, correction for the meniscus, and correction for loss on walls of apparatus, etc. The method gave results comparable with those obtained by drying the coal at 100° C in a current of dry nitrogen

²³ See Lessing, R., pp. 65-8 of ref. 8. Teed, P. L., *J. Gas Lighting*, **122**, 744 (1913). Winmill, T. F., *Colliery Guardian*, **111**, 1090 (1916). Gröppel, H., *Chem.-Ztg.*, **41**, 413-4, 431-4 (1917). Staemmler, C., *ibid.*, **54**, 928 (1930). Vetter, F., *Mikrochemie*, **4**, (2), 407-8 (1932). De Waard, S., and van Beek, F., *Chem. Weekblad*, **29**, 598-603 (1932). Eck, F., *Gas- u. Wasserfach*, **76**, 477-8 (1933).

²⁴ Schläpfer, P., *Z. angew. Chem.*, **27**, 52-6 (1914).

²⁵ Graefe, E., *Braunkohle*, **4**, 581-3 (1905-06).

²⁶ Marcusson, J., *Mitt. kgl. Materialprüfungsamt Gross-Lichterfelde West*, **22**, 48-9 (1904); **23**, 58 (1905).

followed by absorption in calcium chloride of the water given off and determination of the gain in weight. The results obtained by the generally accepted loss-in-weight method were lower. Many other scientists have also used this method, and it has found considerable favor, particularly as a research method. Liquids other than xylene have also been used, and many designs of apparatus have been proposed.²⁷

GENERAL COMPARISONS OF METHODS

A number of extensive studies have been made on the problem of water determination since the reports of the joint American and international committees.

²⁷ Myhill, A. R., *Gas J.*, **150**, 21 (1920). Aufhäuser, D., *Chem.-Ztg.*, **46**, 1149 (1922); *Z. angew. Chem.*, **36**, 197 (1923). Delmarcel, G., and Mertens, E., *Bull. fédération ind. chim. Belg.*, No. **1**, 9-18, 109-18 (1922). Mertens, E., *ibid.*, No. **9**, 361-4 (1922). Liese, E., *Chem.-Ztg.*, **47**, 438 (1923). Erdmann, E., *Jahrb. Halleschen Verbandes*, **1924**, 387-90; *Braunkohle*, **23**, 49-56 (1924-25). Schaefer, K., *Chem.-Ztg.*, **48**, 761 (1924). Kreulen, D. J. W., *Chem. Weekblad*, **21**, 174-6 (1924), **23**, 476-7 (1926). Kattwinkel, R., *Chem.-Ztg.*, **50**, 927 (1926). Normann, W., *ibid.*, **50**, 49 (1926). Dolch, M., and Gieseler, K., *Braunkohle*, **27**, 581-7, 608-13 (1928). Tausz, J., and Rumm, H., *Gas- u. Wasserfach*, **71**, 417-20 (1928). Bunte, K., *Trans. Fuel Conf., World Power Conf., London, 1928*, **2**, 467-81 (German), 481-93 (English) (1929); *Gas- u. Wasserfach*, **72**, 124-7 (1929). Casimir, E. E., and Popescu, A., *Inst. geol. României, Compt. rend.*, **13**, No. 2, 1-18 (1929). Faber, A., *Z. angew. Chem.*, **42**, 406-7 (1929). Mikulina, N. V., Korelin, A. I., and Shakhno, A. P., *Izvest. Vsesoyuz. Teplotekh. Inst.*, **1932**, 933-50. Pieters, H. A. J., and Koopmans, H., *Chem. Weekblad*, **29**, 509-13 (1932). Stansfield, E., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 125-43 (1932). Zikeev, T. A., and Podzharskaya, D. A., *Trans. Thermo-Tech. Inst. (Moscow)*, **1934**, No. 2, 31-4; *Zavodskaya Lab.*, **1**, No. 11/12, 18-22 (1932). Pieters, H. A. J., and Smeets, G., *Het Gas*, **53**, 322-5 (1933). Shakhno, A. P., *Zavodskaya Lab.*, **3**, 198-201 (1934). Wood, W. H., *Combustion*, **7**, No. 2, 16 (1935). Alexander, H. B., *Ind. Eng. Chem., Anal. Ed.*, **8**, 314 (1936). Thielepape, E., and Fulde, A., *Z. Wirtschaftsgruppe Zuckerind., Tech. Tl.*, **87**, 333-42 (1937).

In 1914, Hinrichsen and Taczak²⁸ tested the following eight methods of determining water in coal:

1. Drying in an open flat crucible in air in an oven at 105° C for 1 hour.
2. Drying in a covered crucible in air in an oven at 105° C for 1 hour.
3. Drying in an open flat crucible in an oven filled with carbon dioxide at 105° C for 1 hour.
4. Drying in a crucible set in a beaker which was kept filled with carbon dioxide in an oven at 105° C for 1 hour.
5. Distillation in toluene.
6. Distillation in xylene.
7. Distillation in cumene.
8. Heating to 100° C in an open crucible in a vacuum oven for 1 hour.

The highest results were obtained by method 8, and the next highest by method 6. Hinrichsen and Taczak attributed the higher results obtained by heating in a vacuum to the loss of noncondensable gases and recommended the xylene distillation method. Apparently they made no attempt to distinguish between the moisture and permanent gases given off in a vacuum.

Broche tried the methods of drying samples in air and in carbon dioxide at 105° C as well as distilling in xylene.²⁹ He varied the size of sample, the drying time, and the shape of the drying dish, and he came to the following conclusions: The most exact method is that of distillation with xylene. Drying for 1 hour at 105° C in carbon dioxide gave results that agree with xylene distillation method within limits of accuracy. Drying at 105° C in air is not satisfactory for younger coals but is sufficiently accurate for bituminous coals if the proper procedure is followed, namely, drying a 3-

²⁸ Hinrichsen, F. W., and Taczak, S., *Mitt. kgl. Materialprüfungsamt*, **32**, 283-91 (1914).

²⁹ Broche, H., *Braunkohle*, **26**, 5-9 (1927).

gram sample for 1 hour at 105° C in a flat dish.

The question of determining water in coals has received more attention in Germany than elsewhere because of the great importance of the high-moisture coals of central Europe and the realization of the importance of moisture control in briquetting. In 1929 a prize contest was held by the Deutsche Braunkohlenindustrie Verein and the Mitteldutsche Ostelbische und Rheinische Braunkohlen Syndikat for a quick method applicable to brown coals of 5 to 25 percent water content with an accuracy of ± 0.5 percent. The control analysis was made by means of the xylene distillation method. In all, some 47 different methods were proposed. According to Hirz,³⁰ awards were made as follows: (1) "Deka" method involving measurement of the dielectric constant; (2) "Brikettmeisters-freude" apparatus which heats coal to 150° C and condenses the water and measures the volume; (3) Kubierschky method involving distillation with amyl alcohol; (4) Müller's method of treating brown coal with 40 percent acetic acid and titrating with 0.5 *N* NaOH using phenolphthalein indicator; (5) cold extraction with glacial acetic acid and determination of the conductivity; (6) sulfuric acid method which depends upon heat evolved when coal is dropped into the acid and shaken. The tests of the methods were all made in a single laboratory; both speed and accuracy were given consideration in the award, but time was the essence.

Of considerable interest is a series of experiments on certain coals carried out in a number of technical laboratories and reported by Holthaus.³¹ Two bituminous coals of approximately 0.85 and 5 percent

water content and two brown coals of about 14 and 60 percent water content were prepared as standard samples. Test samples were submitted to seven different laboratories, and many tests were made. The methods tested included (1) xylene distillation according to Erdmann;²⁷ (2) loss in weight on drying at 105° C in drying oven; (3) drying in vacuum by method of Ihlow;¹¹ (4) drying at 105° C and capture of water in reagent; (5) Kubierschky amyl alcohol method (cf. Faber²⁷); (6) cryoscopic method of Dolch and Strube;¹⁴ (7) Zerewitinoff method;¹⁶ and (8) technical method of drying large sample overnight.

Because of the general acceptance of the xylene distillation method abroad, the Erdmann²⁷ technique followed in these tests is described here. For accurate results corrections must be made for buret errors, for meniscus, and for water loss by droplets on walls. Erdmann corrected for meniscus and buret calibration by filling the tube almost to the mark with xylene, dropping in, successively, weighed amounts of water, and reading the meniscus each time. By many control experiments he determined that 99.5 to 100 percent of the known water content is measured. In the Holthaus experiments, calibration was made by distilling weighed amounts of water with xylene. The method of analysis was as follows: 100 grams of bituminous coal was placed in a 500- to 600-milliliter Erlenmeyer flask with 200 milliliters of xylene and well shaken (with brown coal a sample was taken to give about 3 to 6 cubic centimeters of water on distillation). To eliminate hanging up, the apparatus was cleaned with steam, then with sodium bichromate in 80 percent sulfuric acid, then with distilled water followed by steaming for 10 minutes, and finally with dry air. The flask was warmed slowly at the beginning

³⁰ Hirz, H., *Braunkohle*, 28, 101-10 (1929).

³¹ Holthaus, C., *Arch. Eisenhüttenw.*, 5, 149-62 (1931).

so that the first drops of water passed over in 10 minutes, then faster so that 150 cubic centimeters of distillate came over in 45 minutes.

The conclusions from these studies were:

1. The xylene distillation method gives values within limits of accuracy for coals of every water content met in practice. The limits of error were 0.85 ± 0.05 percent, 5.1 ± 0.1 percent, 14.3 ± 0.3 percent, 58.9 ± 0.7 percent.

2. Drying at 105°C in oven is not satisfactory. Coal sorbs air during heating and cooling. With some coals, oxidation and loss of volatile matter also occur.

3. Of all indirect methods, drying in a vacuum and determining loss in weight gives values freest of objection.

4. Satisfactory results can be obtained by drying and sorbing water in phosphorus pentoxide, etc., but the method is cumbersome and hence not recommended.

5. The Kubierschky method is useful for high water content.

6. The cryoscopic method is fast and gives results that check with those by xylene distillation.

7. The magnesium methyl iodide method is not accurate.

8. Drying of a large sample at 105°C overnight meets all industrial requirements of accuracy and speed.

Other, similar series of experiments have been made. Of special interest is that reported by Fieldner, Cooper, and Osgood,³² which gave close checks in results of 25 different laboratories. Circulation of dry air sufficient to change the volume of air in the oven three or four times per minute is necessary for the moisture determination.

Miscellaneous Considerations. The need for a rapid method of reasonable accuracy,

³² Fieldner, A. C., Cooper, H. M., and Osgood, F. D., *U. S. Bur. Mines, Repts. Investigations*, **2432** (1923), 11 pp.

and under some circumstances for a continuous method, has led to the development of special techniques in Germany. Some of these have already been referred to (cf. Hirz³⁰). Others patented and on the market depend on various principles already discussed.³³

Furthermore, there has been a desire to distinguish between surface and other forms of moisture.³⁴ This specialized problem will be touched on in later sections of this chapter.

Air drying of the sample prior to chemical analysis in itself presents a problem, as will be evident from later discussion of the subject, because of the dependence of the moisture content on the humidity as well as the temperature of the drying atmosphere.³⁵

SUMMARY

The problem of the determination of moisture in coal for practical purposes is different in the United States and in continental Europe. Our commercially important coals are of relatively low water content, whereas the high-moisture brown coals of Europe are very important. On the low-moisture coals great accuracy is not so essential if one considers the subject from the standpoint of the dry material. Thus even on a coal with 10 percent water a limit of error of ± 0.5 percent represents an accuracy of almost 0.5 percent on the dry material. The present standard method is generally satisfactory for practical purposes. Chemists realize that the

³³ Brabender, C. W., *U. S. Pat.* 2,047,765 (1936). *Deutsche Erdöl A.-G.*, *Ger. Pat.* 636,316 (1936). *Braunschweigische Kohlenbergwerke und Helmut Platschek*, *Ger. Pat.* 640,347 (1936).

³⁴ Guy, T. W., *Am. Inst. Mining Met. Engrs., Tech. Pub.* **935** (1938), 20 pp.

³⁵ Stansfield, E., *Trans. Can. Inst. Mining Met.*, **26**, 292-7 (1923). Partington, N., *Gas Engr.*, **47**, 27-8 (1930). Davidson, W. B., *Fuel Econ. Rev.*, **9**, 5-14 (1930). Bruere, M., *Ann. fals.*, **24**, 268-73 (1931). McCullough, W. C., *Am. Inst. Mining Met. Engrs., Contrib.* **109** (1938), 4 pp.

results represent a loss in weight under fixed conditions. Moreover, the results can be duplicated with reasonable agreement by different analysts, and a considerable body of useful data has been built up. To attempt to distinguish the different conditions of water in coals would involve procedures that would be relatively complicated and time consuming. Furthermore, much greater care would have to be taken in obtaining the sample. This is generally recognized, as witness the provisions in the A.S.T.M. Standards³⁶ for obtaining special moisture samples.

For research purposes, it is often desirable to determine water with assurance and accuracy. In most instances distillation with xylene, if carefully applied, will serve the purpose, though it should be emphasized that the method is not foolproof. In Europe, particularly in Germany, it has found great favor, a fact which is readily understandable in view of the nature and moisture content of brown coals. However, other special methods will be devised from time to time to serve specific research purposes. Certainly the importance of an accurate estimation of water in coal cannot be overstressed, since many other factors depend on it. Thus it is questionable that an exact estimation of hydrogen in dry coal substance has ever been made, since some of the hydrogen reported for the analysis may have been derived from water in the coal.

THE NATURE AND CLASSIFICATION OF COALS

The role of water in the coalification process and its relation to the nature as well as the classification of coals are still moot questions. Much more experimental investigation, interpretation, and thought

will be required before final answers to these problems are available. Nor are these questions merely of academic interest, because answers to many practical problems would be available if the complete story of the role of water in coal were known.

Water and coal form both mechanical and physical mixtures. Thus part of the water occurring in coal may be termed "free" water; this part has a normal vapor pressure and may be removed by purely mechanical processes. Part of the water, on the other hand, termed "bound" water, constitutes one component of a physical mixture. This water has a vapor pressure lower than normal and a lower specific heat, Kopp's rule not holding.³⁷

Various terms have been used by investigators to differentiate between "free water" and other forms of water in coal. Thus one finds the terms "inherent," "hygroscopic," "bound," and "combined" used by many authors, either interchangeably or with no very definite distinctions between them, or sometimes with empirical definitions given.^{3,38} Vondracek emphasized that there is no satisfactory way of determining the hygroscopicity of coal.³⁹ Gauger³⁷

³⁷ Porter, H. C., and Taylor, G. B., *J. Ind. Eng. Chem.*, **5**, 289-93 (1913). Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper 113* (1916), 28 pp. Coles, G., *Colliery Guardian*, **126**, 973-4 (1923); *J. Soc. Chem. Ind.*, **42**, 435-9T (1923). Gauger, A. W., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 148-61 (1932).

³⁸ Kossmann, B., *Oesterr. Z. Berg- u. Hüttenw.*, **37**, 471-74 (1889). Richters and Muck, cf. Hinrichsen, F. W., and Taczak, S., p. 107 of ref. 22. Kempf, R., *Mitt. kgl. Materialprüfungsamt*, **37**, 178-227 (1920). Kammerer, V., and Guth, J., *Fuel*, **2**, 339-43 (1923). Mott, R. A., *Trans. Fuel Conf., World Power Conf., London, 1928*, **1**, 341-58 (1929). Iki, S., *J. Soc. Chem. Ind. Japan*, **32**, Suppl. Binding 371-2 (1929). Koda, R., *Proc. World Engr. Congr., Tokyo, 1929*, **32**, 269-70 (1931). Matschak, H., *Braunkohlenarch.*, No. **44**, 46-9 (1936).

³⁶ *Am. Soc. Testing Materials, Standards, 1939*, Pt. III, p. 14.

³⁹ Vondracek, R., *Trans. Fuel Conf., World Power Conf., London, 1928*, **1**, 281-4 (1929).

stated that "water recoverable from coal is obtained from the following sources: (1) decomposition of organic molecules (sometimes called 'combined' water); (2) surface adsorbed water; (3) capillary condensed water; (4) dissolved water; and (5) water of hydration of inorganic constituents of the coal." These, of course, are in addition to mechanically admixed water. One must frankly admit that there is at present no method of distinguishing between the amounts of water existing in coal in these various ways.

VAPOR PRESSURE OF WATER IN COALS

The most important technique in the study of water in coal has been the determining of the vapor pressure at varying water contents. In general, the procedure involves either the direct measurement of the vapor pressure of water at different water content of the coal or the equilibration of the sample with controlled humidities.⁴⁰ Typical results obtained by studies of the vapor-pressure-moisture content relationships of coals, lignites, and other materials are shown in Fig. 1. The hysteresis in the curves is particularly noteworthy.

Comparison of the results obtained on lignite with the work of van Bemmelen, Zsigmondy, Anderson, and others indicates that lignites and coals retain part of their

moisture in much the same way that peat, wood, charcoal, and silica gel do.⁴¹ The abnormal vapor pressures as well as the hysteresis may be explained if it is assumed that coals consist in part of a colloidal mass with the properties of a nonswelling gel. Such a structure was proposed for German brown coal by Winter in 1913 on the basis of certain optical properties.⁴² If it is conceded that the colloidal ground mass has a spongelike structure with capillaries of varying radii, these capillaries may be considered as holding liquid water, the meniscus being concave towards the vapor. This will account for the lowering of the vapor pressure.

Since the phenomenon is much more pronounced in the lower-rank coals, the gel structure may be discussed on this basis. A freshly mined lump of lignite loses moisture very rapidly upon exposure to the atmosphere because much of the water is but loosely bound. The vapor pressure of this moisture is equal to that of a plane surface or, in other words, is normal. Upon further loss of moisture, the vapor pressure

- ⁴⁰ Moore, B., and Sinnatt, F. S., *J. Chem. Soc.*, **123**, 275-9 (1923). Moore, B., *J. Soc. Chem. Ind.*, **44**, 200-5T (1925). Raithel, K., *Braunkohlenarch.*, No. **16**, 1-77 (1927). Kreulen, D. J. W., and Ongkiehong, B. L., *Brennstoff-Chem.*, **10**, 317-21 (1929). Lavine, I., and Gauger, A. W., *Ind. Eng. Chem.*, **22**, 1226-31 (1930). Larian, M., Lavine, I., Mann, C. A., and Gauger, A. W., *ibid.*, 1231-34 (1930). Gauger, A. W., ref. 37. Gordon, M., Lavine, I., and Harrington, L. C., *Ind. Eng. Chem.*, **24**, 928-32 (1932). Stansfield, E., and Gilbert, K. C., ref. 27. Krainer, H., *Braunkohle*, **32**, 937-41 (1933). Kühn, H., *ibid.*, **33**, 321-3 (1934). Sauberich, K., *Braunkohlenarch.*, No. **48**, 1-21 (1937). Rees, O. W., Reed, F. H., and Land, G. W., *Illinois State Geol. Survey, Rept. Investigations*, **38**, 1-28 (1939).
- ⁴¹ Van Bemmelen, J. M., *Z. anorg. Chem.*, **13**, 233-356 (1897), **18**, 14-36 (1898), **30**, 265-79 (1902). Zsigmondy, R., *ibid.*, **71**, 356-77 (1911). Zsigmondy, R., Bachmann, W., and Stevenson, E. F., *ibid.*, **75**, 189-97 (1912). Bachmann, W., *ibid.*, **79**, 202-8 (1913). Anderson, J. S., *Z. physik. Chem.*, **88**, 191-228 (1914). Allmand, A. J., Chaplin, R., and Shiels, D. O., *J. Phys. Chem.*, **33**, 1151-60 (1929). Allmand, A. J., and Hand, P. G. T., *ibid.*, **33**, 1161-66 (1929). Allmand, A. J., Hand, P. G. T., Manning, J. E., and Shiels, D. O., *ibid.*, **33**, 1682-93 (1929). Allmand, A. J., Hand, P. G. T., and Manning, J. E., *ibid.*, **33**, 1694-1712 (1929). Pidgeon, L. M., and Maass, O., *J. Am. Chem. Soc.*, **52**, 1053-69 (1930). Hawley, L. F., *U. S. Dept. Agr., Tech. Bull.* **248** (1931), 34 pp. McBain, J. W., Porter, J. L., and Sessions, R. F., *J. Am. Chem. Soc.*, **55**, 2294-304 (1933). Barkas, W. W., *Proc. Phys. Soc. (London)*, **48**, 1-17 (1936).
- ⁴² Winter, H., *Glückauf*, **49**, 1406-13 (1913), **50**, 445-9 (1914). Thiel, G., *ibid.*, **50**, 88-96 (1914). Hinrichsen, F. W., and Taczak, S., p. 182 of ref. 22. Agde, G., and Vetter, K. E., *Braunkohle*, **37**, 135-8 (1938).

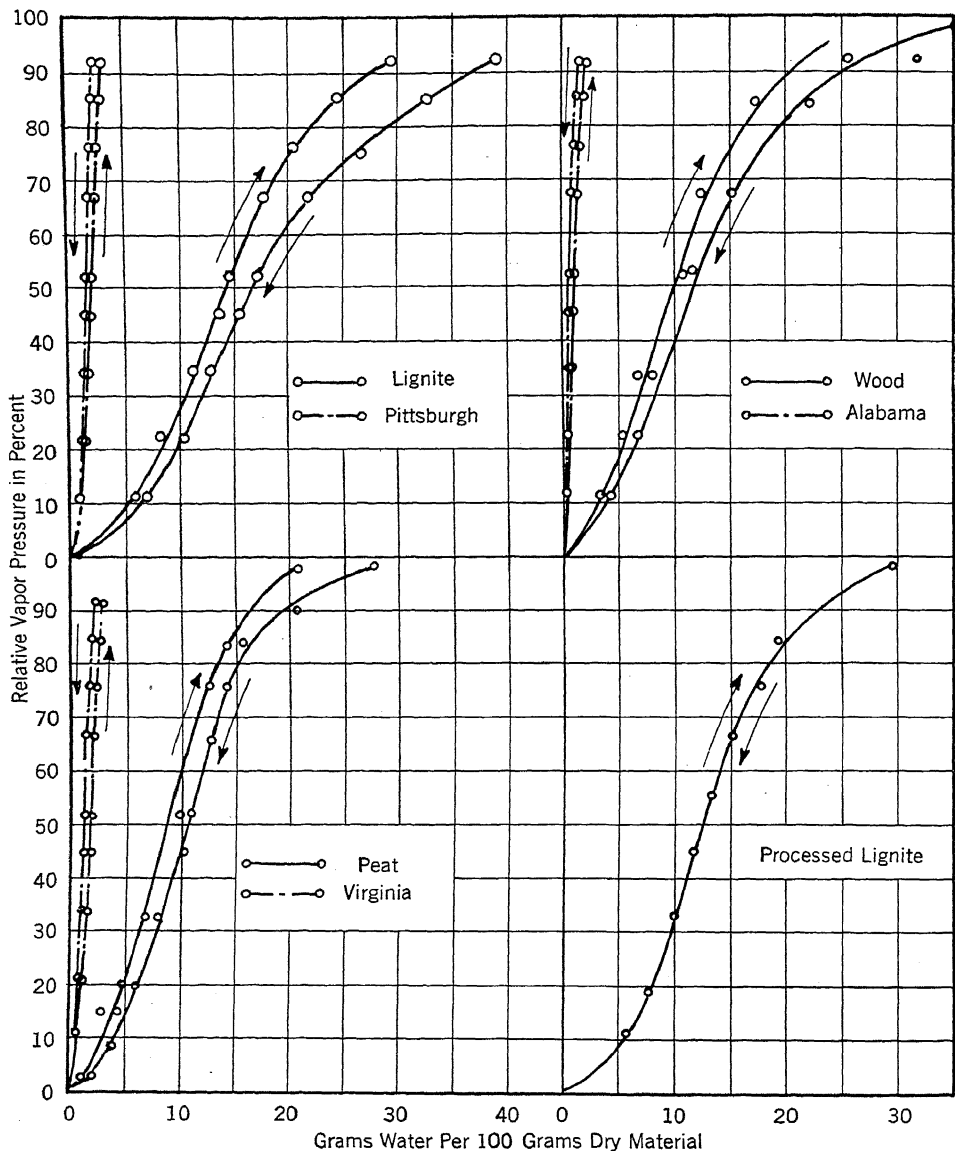


FIG. 1. Typical curves for coals, lignites, peat, and wood showing the relationship of moisture content to relative vapor pressure (Gauger²⁷). Analyses:

	MOISTURE percent	VOLATILE MATTER percent	FIXED CARBON percent	ASH percent	CALORIFIC VALUE Btu
Lignite	35.6	27.9	30.9	5.6	7,110
Pittsburgh	1.2	35.7	58.7	4.4	14,430
Virginia	1.7	36.1	59.5	2.7	14,770
Alabama	1.2	27.9	55.0	15.9	12,600
Processed lignite	9.3	39.8	47.7	5.8	10,000

decreases, which may be explained on the assumption that water is beginning to evaporate from the capillaries. As the water is removed from smaller and smaller capillaries, it may be shown on purely thermodynamic grounds that the vapor pressure of the concave surface must be lowered.

In fact, it is possible by means of the well-known Thomson⁴³ equation to calculate the radii of the capillary spaces in lignite if we assume that the thickness of the adsorbed layer is not too large a fraction of the capillary diameter. By calculating successively the percentage of water held in the pore radii, intervals between the smallest radius corresponding to 100 percent relative humidity ($> 56.73 \times 10^{-7}$ centimeter) and all the other radii, an esti-

mate of the relative distribution of the pore sizes is obtained. These calculations have been made for the samples tested for which data have been given in Fig. 1 and are summarized in Table I. Figure 2 shows the distribution graphically.

From a study of Table I certain tentative conclusions may be drawn with reference to the formation and structure of lignite and other coals. In going from wood to peat it is observed that the relative volume of large capillaries increases. This is evidenced by the fact that over 50 percent of the water in peat is held in capillaries larger than 6.20×10^{-7} centimeter, whereas only 41.8 percent of the water in wood is held in capillaries of similar size. On the contrary, however, in comparing peat with lignite and the bituminous coals examined, a progressive decrease in the relative volume of capillaries of the larger sizes is observed. When the change in water content

TABLE I
MOISTURE HELD WITHIN VARIOUS PORE RADII INTERVALS³⁷

Bound Water *							
Relative Humidity	Radius	Wood	Peat	Lignite	Ala.	Va.	Processed Lignite
percent	cm $\times 10^{-7}$				cumulative percent		
98.0	> 56.73	7.8	18.2	14.8	1.6	2.4	10.2
90.0		25.7	44.7	38.5	15.2	16.8	27.6
84.0	> 6.20	41.8	52.9	44.3	30.4	20.4	39.3
79.2	> 4.65	46.1	55.9	47.7	34.6	26.8	42.6
76.0	> 3.93	49.3	58.2	49.4	38.7	30.8	44.0
66.0	> 2.60	57.9	62.9	54.1	50.8	38.4	52.3
52.0	> 1.65	68.3	68.5	61.8	59.7	45.6	59.1
45.0	> 1.35	71.3	70.6	66.6	61.2	47.6	62.9
33.0	> 0.97	76.5	76.9	75.9	69.1	56.0	66.8
20.0	> 0.67	78.6	82.9	81.8	80.6	63.6	75.0
14.9	> 0.57	85.7	87.1	85.9	82.7	73.2	78.5
9.2	> 0.45	89.5	88.5	89.6	86.9	80.0	83.3
3.5	> 0.32	95.0	94.0	92.5	94.2	90.8	91.8
0.0	> 0.00	100.0	100.0	100.0	100.0	100.0	100.0

* Percentage of bound water = $\frac{T - E}{T} \times 100$, where T = moisture at 100 percent relative humidity, and E = moisture at any other humidity.

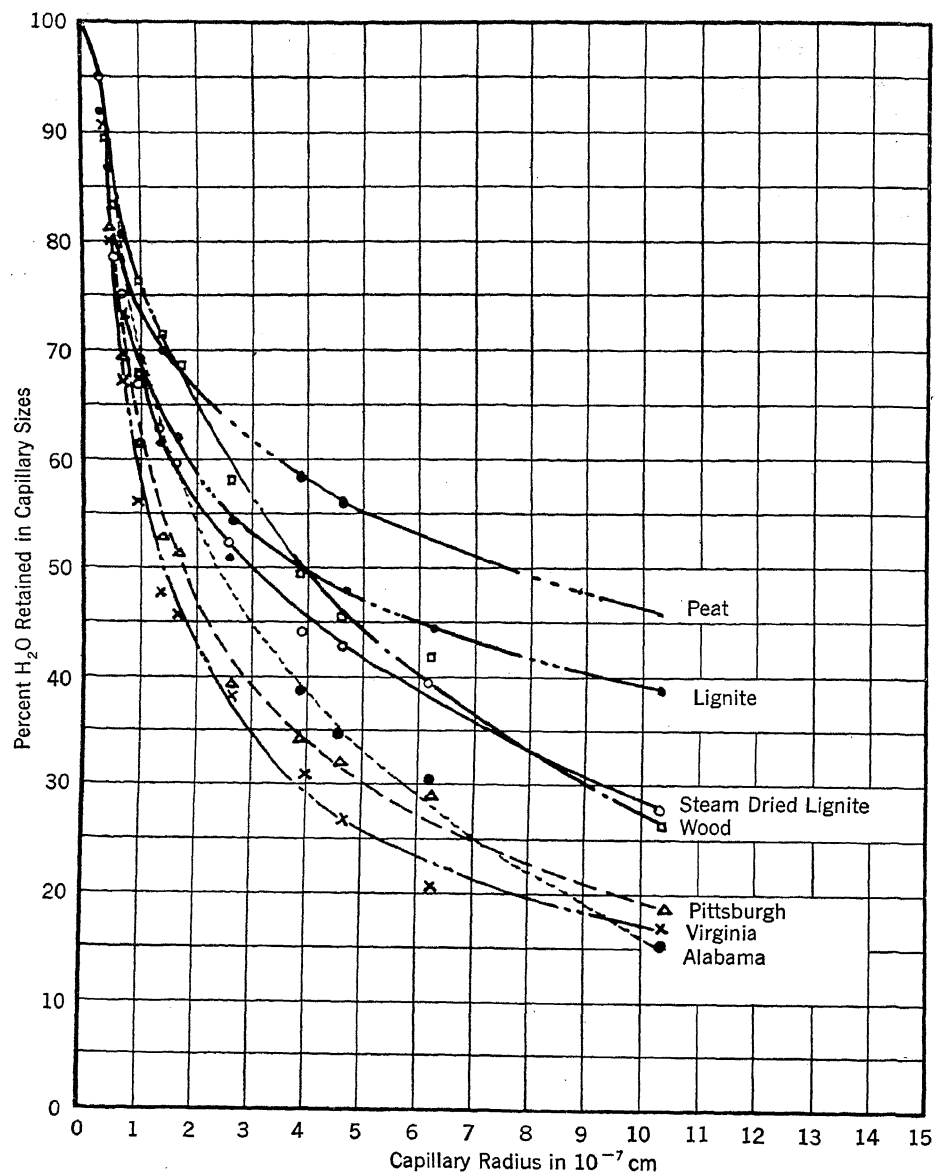


FIG. 2. Moisture retained as a function of capillary radius for coals, lignites, peat, and wood (Gauger ²⁷).

during the coalification process is also considered, it becomes evident that there has been an increase in pore volume in going from wood to peat, and a progressive decrease in pore volume from peat to bituminous coal. At the same time, in the transformation of wood to peat there has been a relatively larger increase in the percentage volume of large capillaries, whereas in the later stages of the coalification process the decrease in the percentage volume of large capillaries overshadows the decrease in that of small capillaries.

During the transformation from wood to peat, biological and chemical decay take place, resulting in the formation of a hydrosol in which the larger portion of the water content is contained in capillaries of diameter larger than 6×10^{-7} centimeter. In other words, the formation of peat from wood is accompanied by swelling and an increase in volume of large capillaries, no doubt due in part to biological causes. As the process goes on with the aid of pressure, the small pores and openings undergo but slight decrease in size. On the other hand, the large openings decrease materially. Water is lost, and the mass becomes a hydrogel. As the coalification process proceeds to the coals of higher rank, there is a continual decrease in the capillaries of all sizes, but especially the large ones. In consequence, the moisture isotherm is shifted more markedly to the left in the region of higher vapor pressure.

This phenomenon is brought out very distinctly in the effect of partly dehydrating lignite by means of saturated steam at high pressure. In this process⁴⁴ lignite is exposed to saturated steam at a pressure of 13 atmospheres or more for a suitable length of time. The pressure is then released and warm air is blown through the

mass. When removed, the lignite has dried to about 15 percent water, at the same time retaining its original form value. Such processed lignite will dry to a lower moisture content than raw lignite under similar conditions. The curve for processed lignite in Fig. 1 indicates not only that there has been a distinct loss in the relative volume of larger capillaries, but that the phenomenon of hysteresis has almost disappeared. In other words, apparently this is an example of reversible sorption. However, the desorption and sorption graphs do not represent equilibrium conditions when dealing with lower-rank coals. Consequently, it is not strictly accurate to speak in this connection of the vapor pressure of a low-rank coal, inasmuch as the same value cannot be reached from both sides.

The phenomenon of hysteresis occurs in many cases of sorption. No generally accepted explanation is yet available, but in respect to lignite it can be explained on two assumptions: (1) the shrinking of lignite upon drying causes a collapse of some of the capillaries, and the dried material can no longer take up as much water as it held originally; (2) the replacement of moisture on the walls of some of the capillaries by adsorbed gases makes it difficult to wet the capillaries. As a result, the diameter of the surface of the water in the capillary is diminished and the vapor pressure at any given water content decreases accordingly. The behavior of the steam-dried lignite is considered good evidence in favor of the collapse of capillary theory. In this process, the colloidal mass has been set and further permanent shrinkage does not occur upon complete dehydration. The effect of oxygen on the coal surface cannot be neglected; hysteresis was found whether the de- and rehydration

⁴⁴ Lavine, I., Gauger, A. W., and Mann, C. A., *Ind. Eng. Chem.*, **22**, 1347-60 (1930).

took place in the presence of air or in a vacuum.

The coalification process appears to have a similar effect on lignite, for the higher-rank coals, if anything, appear to take up slightly more water upon rehydration. In other words, the hydration curve lies outside the dehydration curve. This phase of the problem requires further study by more refined methods, because the larger values might also be explained by adsorption of oxygen and nitrogen from the atmosphere. In connection with the high-moisture coals this factor is negligible, but it becomes increasingly important as the moisture content of the coal decreases.

With reference to the comparatively large quantity of water still retained by coals after drying over sulfuric acid at ordinary temperatures and atmospheric pressure, the meager evidence now available indicates that water given off in a vacuum at temperatures between 100 and 200° C consists mainly of adsorbed water. At some temperature above that point decomposition sets in, liberating what has been termed chemically "combined" water. It is hardly likely that such water is present as water of hydration of the organic compounds that make up the coal substance. It is more reasonable to assume that the decomposition of compounds containing carboxyl groups results in a splitting off of water. Nor does it seem unreasonable to assume that a small fraction of the water considered, on the basis of vapor-pressure studies, as being condensed in capillaries really consists of surface adsorbed water. If one accepts the Langmuir⁴⁵ mechanism for adsorption of gases on solid surfaces as being applicable to the adsorption of water vapor on coal surfaces, the process is a dynamic one and water

molecules are condensing on and evaporating off the surface at all times. In consequence of this mechanism, as well as surface changes due to shrinkage, adsorption of gases, and other factors, the progressive drying of the coal at the lower relative humidities may remove some adsorbed water. Further study is necessary in order to distinguish accurately the types of mechanism by which water is retained by coal.

Agde⁴⁶ and his coworkers believed that it is impossible to distinguish between the extraction of the capillary water and the adsorbed layer (that is, on the solvation surface). Berl and Immel,⁴⁷ on the other hand, led by the thought that these surfaces are in part hydrophilic and in part hydrophobic, found it possible to extract water from the inner surface by means of aniline, cresol, and other bipolar oils, and to remove it by pressing. All these studies, of course, refer to low-rank coals.

Rosin, Rammmler, and Kayser have made careful mathematical analyses of data on vapor-tension studies from various sources.⁴⁸ Rosin and his coworkers proposed a general equation for the vapor-pressure isotherms of swelling gels as follows:

$$\phi = 100(1 - e^{-bx^n})$$

where e is the base of natural logarithms, x is the water content on dry basis in percent, ϕ is the relative vapor pressure in percent, and b and n are constants. This equation has been tested by the author on the data of Rees, Reed, and Land (cf. ref. 40) and found to hold reasonably well.

⁴⁶ Agde, G., and Hubertus, R., *Braunkohle*, **31**, 675-80 (1932).

⁴⁷ Berl, E., and Immel, A., *Kolloidchem. Beihefte*, **24**, 181-267 (1927).

⁴⁸ Rosin, P., Rammmler, E., and Kayser, H. G., *Braunkohle*, **33**, 289-94, 305-14 (1934).

⁴⁵ Langmuir, I., *J. Am. Chem. Soc.*, **38**, 2221-95 (1916).

Similar treatments have been proposed by others.⁴⁹

With reference to the phenomenon of hysteresis, Rosin made the following comments:

In gels one designates as hysteresis the phenomenon that, with equal relative vapor pressure, a lower content is found if the gel is being loaded with water compared to the water contents if water is removed. As cause for this, Zsigmondy has suspected wetting difficulties in the pore structure. These are supposed to be caused by a change of the interior surface of a gel through adsorption of gases, which, however, is not true for the removal of water from the capillary structure which has not come in contact with gases. Recently Kubelka has reasoned from investigations of active carbons which cannot be considered as swelling gels that not wetting difficulties, but rather superheating of the vapor phase, is to be considered the cause of hysteresis phenomenon without being able to substantiate this deduction more closely. One may, therefore, say that the cause for the hysteresis of coal is as yet unknown. However, the affinity of the coal for oxygen is evidence for a change of the capillary structure taking place under drying conditions in the presence of oxygen which one might think of as an aging of the capillary walls and that, therefore, the explanation of Zsigmondy covers part of the phenomenon. One might obtain better clarification if planned investigations on the dependence of the hysteresis on the drying atmosphere (carbon dioxide, nitrogen, oxygen) and the temperature were initiated. In using Fleissner drying, the hysteresis disappears completely according to the North Dakota experiments. In treatment with vapor, the pore structure shrinks before the vapor pressure isotherm is determined.

The assumption that the hysteresis phenomena are due to wetting difficulties because of preadsorption of gases and because of nonuniform chemical properties of the adsorbing surface (for example, nonactive surface parts at high ash contents) has been strengthened by new investigations of low-

temperature coke.⁵⁰ By heating in a vacuum, activated low-temperature coke adsorbs larger quantities of water at the same vapor pressure than does preoxidized low-temperature coke. These investigations have also shown that the wetting processes in the case of hysteresis phenomena belong to that group of processes which are composed of single phases overlapping each other in discontinuous fashion.

THE COALIFICATION PROCESS

The role of water in the coalification process has been given consideration by a number of scientists.⁵¹

It is generally accepted that coals of the common kind, regardless of rank, are evolved from peat. In the formation of peat, the initial role of water is to envelop the vegetable debris and exclude atmospheric oxygen. This impedes, arrests, or modifies the processes of decay. David White believed that climatic conditions of drought or rainfall had a profound effect on the progressive change of the organic debris.⁵²

Although it must be admitted that the inevitable presence of water, acting as a solvent, as a carrier of debris, and in many other ways, must have been a factor in the coalification process, it seems doubtful that it will ever be possible to distinguish its role as an independent factor in this process.

⁵⁰ Agde, G., and Hubertus, R., *Braunkohle*, **32**, 65-68, 87-91 (1933).

⁵¹ Stevenson, J. J., *Proc. Am. Phil. Soc.*, **50**, 1-116, 519-643 (1911), **51**, 423-553 (1912), **52**, 31-162 (1913), **53**, 21-203 (1916), **56**, 53-151 (1917), **57**, 1-48 (1918), **59**, 405-511 (1920). White, D., Thiessen, R., and Davis, C. A., *U. S. Bur. Mines, Bull.* **38** (1913), 390 pp. Jeffrey, E. C., *J. Geol.*, **23**, 218-30 (1915); *Mem. Am. Acad. Arts Sci.*, **15**, No. 1 (1924), 62 pp. Armstrong, H. E., *Proc. Roy. Soc. (London)*, **127**, 268-71 (1930). Hickling, G. A., *Can. Mining J.*, **52**, 428-9 (1931); *Proc. S. Wales Inst. Engrs.*, **46**, 911-51 (1931).

⁵² White, D., *Econ. Geol.*, **28**, 536-70 (1933).

⁴⁹ Vondracek, R., and Mosendz, L., *Collection Czechoslov. Chem. Commun.*, **3**, 81-92 (1931). Kubelka, P., *Kolloid-Z.*, **55**, 129-43 (1931).

CLASSIFICATION OF COALS

In a consideration of the classification of coals it is now generally accepted that water cannot be neglected in the lower-rank coals. Ashley, for example, considered that the moisture content within limits is a characteristic of the coal and proposed calculation of the analysis for classification to a standard ash content of 7 per cent and moisture at 20° C and 15 millimeters pressure of mercury aqueous tension.⁵³ Other authors have concluded that for low-rank coals it is essential to determine the natural bed moisture. If a sample with natural bed moisture is not available, methods of equilibration which depend upon extrapolation of vapor-pressure isotherms to determine the bed moisture have been proposed (cf. Stansfield and Gilbert, ref. 27). It is difficult to see how such methods can be reliable in view of the hysteresis phenomenon and the general dependence of the moisture content on the previous history of the sample.⁵⁴ Rees, Reed, and Land found the equilibrium method to give erratic results with Illinois coal.⁴⁰

The American Standards Association Committee on Coal Classification after a study of some ten years concluded that it was necessary to classify coals of high-volatile B bituminous coal rank and lower on the basis of natural bed moisture.⁵⁵ Seyler did not concur in this view.⁵⁶ Later discussions on the effect of moisture on the physical properties of lignites and sub-bituminous coals will illustrate the need for such consideration of natural bed moisture.

⁵³ Ashley, G. H., *Trans. Am. Inst. Mining Met. Engrs.*, **65**, 782-94 (1919-20); *Coal Industry*, **7**, 15-8 (1924).

⁵⁴ Kempf, R., *Mitt. kgl. Materialprüfungsamt Berlin-Lichterfelde West*, **37**, 178-227 (1920).

⁵⁵ *Am. Soc. Testing Materials, Standard Spec. D388* (1938).

⁵⁶ Seyler, C. A., *Proc. World Engr. Congr., Tokyo*, **32**, 271-85 (1929).

SUMMARY

Water and coal form both mechanical and physical mixtures. The water in the physical mixture has a vapor pressure lower than that of free water. Vapor-pressure studies on the lower-rank coals indicate that coals may be looked upon as colloidal masses with the properties of a nonswelling gel. Distinction between the amount of water retained in the coal by the various mechanisms cannot be made in the present state of our knowledge. Water undoubtedly played an important part in the coalification process, but its role as an independent factor in this process cannot be determined. Since water is an essential component of lignites and certain low-rank coals, it is desirable to consider the natural bed moisture in any system of classification of coals.

STORAGE AND UTILIZATION OF COALS

SLACKING OR WEATHERING

The effect of moisture on coals during storage and transportation is distinctly more pronounced for the lower-rank than for the higher-rank coals. In fact, the effects of drying, or of alternate drying, wetting, and drying, on the physical properties and structure of the subbituminous and lignite coals are so marked as to be distinguished by the terms "weathering," or "slacking," which is a recognized characteristic in the classification of coals by rank.

A freshly mined lump of lignite is a compact, tough, hard material which can be broken only with difficulty. If the lump is exposed to the dry atmosphere of a warm room in winter, it checks and cracks until finally the original tough block, which was split with difficulty by an axe, has degraded into a pile of brittle pieces so friable as to crumble under pressure of

the fingers. The sole difference of the before-and-after specimens detected by chemical analysis is a decrease in the moisture content from upwards of 30 to under 20 percent. As the block lost water, its physical character changed completely, and the residue, though higher in heating value, lost the form value of the original.

In coals of higher ranks this property becomes less pronounced until in the coking coals it appears to be lost entirely. Since there is no sharp discontinuity in this property, it becomes necessary to devise a test method in order to distinguish between borderline cases. Fieldner, Selvig, and Frederic⁵⁷ have proposed such a method which, with slight modification, is used for classification purposes according to the A.S.T.M. Specification D388-38. The test consists of air drying 500 to 1,000 grams of 1- to 1.5-inch lumps at a temperature of 30 to 35° C and a humidity of 30 to 35 percent for a period of 24 hours, followed by immersion of the lumps in water for 1 hour; the water is then drained off and the sample again air dried as above for 24 hours. The sample is then sieved on a wire mesh sieve with 0.263-inch square openings, and the undersize and oversize are weighed. A blank sieving test on the original coal is also made. The undersize from the slacked sample is the weathering or slacking index of the coal.

The proposed slacking test has been criticized as "misleading and erroneous."⁵⁸

⁵⁷ Fieldner, A. C., Selvig, W. A., and Frederic, W. H., *U. S. Bur. Mines, Repts. Investigations*, **3055** (1930), 24 pp.

⁵⁸ Stansfield, E., Lang, W. A., Sutherland, J. W., Gilbert, K. C., and Zeavin, S., *Sci. Ind. Research Council, Alberta, Can., 9th Ann. Rept.*, **1928**, 15-9. Parr, S. W., and Mitchell, D. R., *Ind. Eng. Chem.*, **22**, 1211-2 (1930). Stansfield, E., and Gilbert, K. C., *Am. Inst. Mining Met. Engrs., Tech. Publ.* **543** (1934), 8 pp. Nicolls, J. H. H., Can. Dept. Mines, mimeographed paper entitled "Studies of the 'True' Moisture and

Parr and Mitchell claimed that slacking is not a fixed and definite function of the coal. In lignites, the slacking is "due to the wetting and not the drying process, and the disintegration is substantially 100 percent complete after one complete cycle." The experience of the writer with lignites indicates that lignites disintegrate to a very marked degree on the initial drying. The question, therefore, seems to hinge on the definition of the degree of disintegration. Parr and Mitchell considered slacking tests inapplicable to bituminous coals as an indication of rank and pointed out that fusain layers and clay bands are also not without influence on the weathering of coals.

Other writers have pointed out the effect of oxidation in storage on the weathering of coal. Weathering, of course, is an oxidation process, and there is evidence that the amount of combined water in the coal is increased thereby.⁵⁹

Freezing. The freezing of coals as a result of the presence of free water has also been the subject of investigation. Sakhareenko reported that Moscow coals with 22 to 24 percent water did not freeze, and hence concluded that this water was in chemical combination. With greater mois-

'Pure-Fuel' Calorific Values of Selected Canadian, United States and Other Coals," 1935, 32 pp.

⁵⁹ Richters, E., *Dinglers Polytech. J.*, **195**, 315-31, 449-58 (1870), **196**, 317-35 (1870). Fischer, F., *Z. angew. Chem.*, **24**, 564-9, 787-90 (1899). Parr, S. W., and Hamilton, N. D., *Illinois State Geol. Survey, Bull.* **8**, 196-204 (1907). Parr, S. W., and Wheeler, W. F., *ibid.*, **8**, 167-75 (1907). Porter, H. C., and Ovitiz, F. K., *J. Ind. Eng. Chem.*, **4**, 5-8 (1912). Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper* **65** (1914), 30 pp. Porter, J. B., et al., *McGill Univ. and Can. Dept. Mines, Bull.* **33S** (Supplementary Bull. **83**) (1915), 194 pp. Parr, S. W., and Milner, R. T., *Fuel*, **5**, 298-301 (1926). Parr, S. W., *ibid.*, **5**, 301-5 (1926). Kattwinkel, R., *Teer*, **25**, 197-200 (1927). Gilmore, R. E., and Strong, R. A., *Trans. Can. Inst. Mining Met.*, **36**, 317-70 (1933).

ture content, freezing appeared to take place.⁶⁰

SPONTANEOUS IGNITION

A second important phenomenon in connection with storage of coal is that known as spontaneous combustion. Katz and Porter and also Tideswell believed that the rate of oxidation of different coals is not uniformly affected by moisture. Wetting may, however, bring about physical changes and modify the ventilation conditions in the pile.⁶¹

There seems no doubt but that moisture and oxygen sorption are in some manner interrelated, and consequently moisture affects the tendency to spontaneous combustion. Moreover, the heat of wetting is, particularly in high-moisture coals (of low-rank), not inconsiderable.

Porter and Ralston³⁷ showed that heat is produced by wetting dry coal or partly dried coal containing less than its normal percentage of water. To quote from their paper, "The relative quantity of heat generated depends on the kind of coal and its relative deficiency in inherent water as referred to its maximum normal content. In other words, the thermal effect of wetting varies directly as some function of the relative vapor-pressure deficiency in the coal." Porter and Ralston considered as "inherent water" all water that did not exhibit normal vapor pressure; the term, therefore, includes adsorbed water as well as capillary condensed water.

The functional relationship between vapor pressure and heat of vaporization may be obtained from the Clapeyron-Clau-
sius equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

in which ΔH is the heat of vaporization of the water, T the absolute temperature, ΔV the change in volume on vaporization, and dp the change in vapor pressure. This requires isotherms at two different temperatures. Lavine and Gauger⁴⁰ assumed that ΔH may be considered a constant and that the ideal gas laws hold under these conditions; they calculated the heat of vaporization of capillary water from lignite between 10 and 40 grams of water per 100 grams of dry lignite. Their results are reproduced in Table II.

TABLE II

HEAT OF VAPORIZATION OF MOISTURE FROM LIGNITE

$$ML = 2.303R \frac{T_1 \cdot T_2}{\log_{10} \frac{P_2}{P_1}}$$

where $ML = \Delta H$ = molecular weight multiplied by latent heat of vaporization in calories per gram; R = gas constant; P_1 and P_2 = vapor pressures at absolute temperatures T_1 and T_2 , respectively.

Moisture per 100 Grams Dry Lignite	Pressure		Heat of Vaporization calories per gram
	At 20° C	At 40° C	
	centimeters of mercury		
grams			
40	1.653	5.355	592.9
35	1.561	5.051	593.8
30	1.433	4.646	594.8
25	1.254	4.099	598.9
20	1.024	3.440	612.8
18	0.737	2.545	626.7
10	0.395	1.411	643.8
			Av. 609.1

Unfortunately, the results of Lavine and Gauger do not lend themselves to a ready comparison with the data of Porter and Ralston, but subtracting the normal heat of vaporization of water from the abnormal results for lignite gives a value which should correspond to the heat of wetting.

⁶⁰ Sakharenko, P. B., *Izvest. Teplotek. Inst.*, 1933, No. 3, 35-41. Mikhailov, N. M., *Trans. Thermo-Tech. Inst. (Moscow)*, 1934, No. 1, 34-41.

⁶¹ Katz, S. H., and Porter, H. C., *U. S. Bur. Mines, Tech. Paper 172* (1917), 22 pp. Tideswell, F. V., *Proc. S. Wales Inst. Engr.*, 36, 183-258 (1920-1); *Gas J.*, 151, 394 (1920).

The average increase in heat of vaporization between 10 and 25 grams of water per 100 grams of dry lignite is about 40 calories per gram of water. Assuming that the same lignite was used by Porter and Ralston in experiments on both the vapor pressure and heat of wetting, one can calculate a heat of wetting of about 60 calories per gram of water over the same moisture range. The order of magnitude is the same, and the lack of better agreement may be attributed to the previous history of the samples in the two different sets of experiments. The heat of adsorption of water vapor on coal surfaces is undoubtedly much larger than the heat of wetting.

MOISTURE IN COMBUSTION

One of the most important uses for solid fuel is in the generation of heat by combustion in furnaces. It is generally accepted by firemen and engineers that some moisture is desirable to promote combustion. Until recently, however, there have been few published data indicating the actual effect on combustion of varying amounts of water. Dunningham and Grumell have carried out a notable series of experiments on the combustion of fuel on a traveling grate.⁶² These experiments showed that the addition of water to fuels which contain a large percentage of fines had the effect of decreasing the resistance of the fuel bed to the air flow. Consequently, as water was added, higher air rates were possible when burning fine coal. These authors stated:

The minimum resistance corresponds to optimum water content, that is to say, the maximum water which can be held by the fuel without drainage occurring on standing. These fuels contain 70 to 80 percent under

$\frac{1}{8}$ inch and require approximately 12 percent free water for minimum resistance. One fuel is coking and the other free-burning, and the fact that the effect of water is purely physical and independent of the chemical properties of the fuel is confirmed by a similar curve for sand. The curve for density of the material indicates that the resistance is linked up with this property.

In other words, the resistance of the fuel bed as related to the water present was also related to the bulk density. Water is also known to be an excellent catalyst for many gaseous reactions involving oxygen. Perhaps an additional effect is in the promotion of the reaction with oxygen of the gaseous products distilled from the coal.

Dunningham and Grumell also showed that the addition of water to coking coal caused smaller pieces of coke to be formed, resulting in a more uniform fuel bed. Furthermore, the initial ignition of the fuel was somewhat retarded, and this effect might be considerable where large additions of water were necessary. The rate of advance of the ignition point through the fuel bed was also slowed down, which would increase the length of the grate in contact with green fuel, and with a reactive free-burning fuel it might cause a center-line fuel bed with possibly an approach state, so that it is essential that the fuel be wet uniformly.⁶³

Matthews⁶⁴ believed that moisture also caused heat generation at the surface of the fuel bed and in the combustion space, owing to strongly endothermic reactions deep in the fuel bed forming hydrogen and carbon monoxide that burn at the surface. He believed also that moisture retarded the rate at which volatile matter was distilled

⁶² Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel*, **9**, 24-9 (1935).

⁶⁴ Matthews, F. J., *Steam Engr.*, **5**, 25-6 (1935). Park, W. M., *Combustion*, **11**, No. 10, 24-8 (1940).

⁶³ Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel*, **12**, 87-95 (1938).

off and, therefore, cut down the danger of smoke occurrence. Park stated that evaporation of extra moisture increases the superheated-vapor item of the stack loss, but this is more than offset by the improvement in carbon dioxide and reduction in ashpit loss.⁶⁴

For pulverized-fuel burning it appears to be essential to dry brown coals and lignites down to about 15 to 20 percent water.⁶⁵

EFFECT ON GRINDABILITY AND SIEVING

Moisture is a factor of greater significance in the high-moisture, low-rank coals than in the high-rank coals. Since brown coal is of considerable economic importance much more work has been done on the effect of moisture in various types of coal testing. Thus Rammmler and Winkler and others have studied the effect of moisture on grindability of brown coal.⁶⁶ In general, the grindability increased as the water content decreased, as would be expected in consequence of the tendency of such coals to slack.

Winkler and Tietze, who studied the sieving of raw brown coal, reported that the sieve capacity decreased with increasing water content.⁶⁷ Other factors such as grain size and nature of the material also had an effect on the results. Obviously, if there is sufficient surface moisture to cause agglomeration, the sieve capacity will be affected adversely, regardless of the rank of the coal. This type of work does not appear to have reached a point of general application.

⁶⁴ Rammmler, E., *Braunkohle*, **25**, 120-31 (1926). Sutherland, R. L., Bourke, N. T., and O'Keefe, E. J., *Power*, **67**, 141-4 (1928).

⁶⁵ Winkler, G., *Braunkohlenarch.*, No. **30**, 1-93 (1930).

⁶⁷ Winkler, G., and Tietze, O., *Braunkohlenarch.*, No. **36**, 56-69 (1932).

VOLUME CHANGE ON DRYING

Several investigators have studied the volume change on drying of brown coal.⁶⁸ In general, the density of brown coal was found to increase as the moisture content decreased until a maximum was reached in the range of 5.0 to 6.9 percent water, after which a small decrease took place.

Rammmler and Augustin have applied such phenomena to a consideration of the drying processes in a suspension. The grain size diminished as the moisture content decreased; consequently, the settling velocity also decreased. Such studies are of importance in the consideration of processes which dehydrate fine brown coal in suspension.⁶⁹

BULK DENSITY

The bulk density of bituminous coals, which is also a function of the moisture content, is of importance in carbonization.⁷⁰ (See also Chapter 23.) Chapman and Barnhart found that with increasing moisture content the bulk density of a coal decreased up to a moisture content of 6 percent. Between 6 and 7 percent (the highest moisture content studied by them)

⁶⁸ Graefe, E., *Braunkohle*, **9**, 177-9 (1910-11). Dolch, M., *Brennstoff- u. Wärmewirt.*, **8**, 333-5, 354 (1926). Pieters, H. A. J., *Het Gas*, **51**, 91-2 (1931). Benade, W., *Braunkohle*, **31**, 845-8, 864-8 (1932). Luikov, A. V., *Kolloid Z.*, **69**, 226-30 (1934), **71**, 103-11 (1935). Šimek, B. G., *Mitt. Kohlenforsch. Inst. Prag*, **2**, 227-33 (1935).

⁶⁹ Rammmler, E., and Augustin, O., *Braunkohle*, **38**, 23-4 (1939).

⁷⁰ Chapman, H. M., and Barnhart, E., *Iron Age*, **51**, 1140 (1908). Drakeley, T. J., and Jones, W. O., *J. Soc. Chem. Ind.*, **42**, 163-6T (1923). Koppers, H., and Jenkner, A., *Glückauf*, **66**, 834-8 (1930); *Fuel*, **9**, 521-6 (1930). Leven, K., *Glückauf*, **67**, 770-2 (1931); *Fuel*, **10**, 369-71 (1931). Pieters, H. A. J., *Het Gas*, **51**, 91-2 (1931). Russell, C. C., *Koppers News*, October, 1931. Stuchey, R., *Tech. Mitt. Krupp*, **4**, 19-21 (1936).

there was little change in the bulk density. They also noted that the magnitude of the decrease in bulk density for the addition of a given percentage of water depended on the amount of fines in the coal. The greatest decrease occurred in the sample having the greatest percentage of fines.

Koppers and Jenkner studied the effect of moisture content on two coals, one 19.1 percent above 1 millimeter in size, the other 46.4 percent above 1 millimeter and very little below 0.2 millimeter. With both coals, the bulk density decreased with increasing moisture content, went through a minimum, and then rose. According to Pieters, the minimum bulk density was obtained at a moisture content of 8 percent. Leven also noted that the initial decrease in bulk density with increase in moisture content was followed by an increase in bulk density at high percentages of water. Working with a coal 100 percent below 0.5 millimeter in size, the minimum bulk density was reached at a water content of 10 percent. Leven considered that the greater air space in moist coal is an advantage in the coking of swelling coals in that it provides more room for the expansion

of the coal charge. In an example given by Russell, the minimum bulk density obtained by the addition of water to a coal was found when the water content was 7.5 percent. However, on calculating the actual amount of dry coal in the container at various moisture contents, the minimum amount of coal was found to be present when the water content was 9.5 percent. Russell remarked that these minima would occur at other moisture contents with coals of different pulverization. Stuchtey studied the effect of moisture on the bulk density of coal samples having different size distributions. The greater the percentage of fines in a sample, the greater the amount of water that had to be added before the minimum bulk density for that sample was reached.

Studies in the laboratories of Pennsylvania State College on the effect of moisture on bulk density indicate that the bulk density decreases as the moisture increases, passes through a minimum, and then increases, although this is not true for all sizes. Data are given in Fig. 3 and Table III.

With the largest size the bulk density of

TABLE III

EFFECT OF MOISTURE ON BULK DENSITY OF COKING BLEND I ($-\frac{1}{4}$ -inch coal) *

Moisture, percent	0.8	3.3	5.8	8.3	10.8	13.3	15.8	18.3	20.8
Bulk density, grams per cubic centimeter	0.76	0.63	0.54	0.52	0.51	0.52	0.52	0.55	0.61
Grams "dry" coal per cubic centimeter	0.75	0.61	0.51	0.48	0.46	0.45	0.44	0.45	0.48

* This blend consists of four coals analyzing as follows:

As received				
	A	B	C	D
Moisture, percent	1.2	1.1	0.9	0.9
Volatile matter, percent	34.1	32.7	29.4	16.7
Fixed carbon, percent	57.9	59.1	62.8	76.4
Ash, percent	6.8	7.1	6.9	6.0
Sulfur, percent	1.0	1.0	1.1	0.8

The blend contained 35 percent of A; 25 percent of B; 20 percent of C; 20 percent of D.

the coal rises slightly with increase in moisture content. Even here the moisture of the coal must have a slight effect on the packing of the coal, for, if it did not, the bulk density would increase in the same percentage as the water content. With decrease in the size of the coal particles, the lowering of the bulk density by the

addition of water becomes more noticeable. The greater difference between the bulk density of wet and dry coal occurs with the intermediate sizes, probably because the fine sizes have a very low bulk density even when dry. With all the different sizes the increase in bulk density at

since the bulk density obtained under such conditions is materially higher than that obtained with addition of water alone.

SURFACE PROPERTIES OF COAL

Brady and Gauger have studied the surface properties of coal with respect to

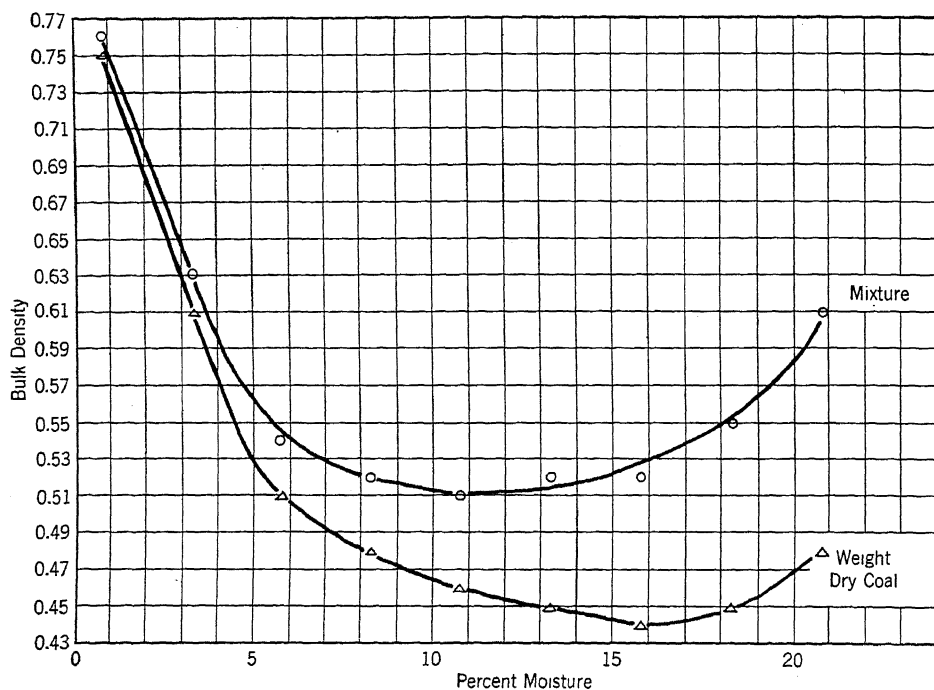


FIG. 3. Bulk density of coal as a function of its moisture content.

high percentages of water was so slight as to be almost negligible.

Studies were made on a single blend of coals coked in a rectangular laboratory oven to determine the effect on coke strength. With the blend studied, increasing the moisture content up to 6 percent decreased the bulk density of the charge, increased the porosity of the coke, and decreased its mechanical strength.

The bulk density of moist coal is highly susceptible to additions of wetting agents

water⁷¹ by measurement of the angle of contact when a surface is wet. Neither nitrogen nor air was found to displace water from a surface of lignite. In higher-rank coals, these authors believed that the affinity of a coal surface for water in preference to air depends to an appreciable extent on which one is first present after the surface is produced. Similarly, for coal-organic-liquid-and-water, the question

⁷¹ Brady, G. A., and Gauger, A. W., *Ind. Eng. Chem.*, **32**, 1599-604 (1940).

of which fluid first came into contact with the surface was of profound importance. This is significant in connection with coal-washing processes employing heavy organic liquids, since, if the coal surface is first wet with water, it will carry away a minimum of the heavy liquid. Also in dustproofing with oil, it should be possible to accomplish the result with less oil if water is first employed to coat the surface. In order to keep the water at a minimum, a wetting agent should be used.

MOISTURE AND CARBONIZATION

The effect of moisture content on the carbonization of coals of all ranks has been studied by several investigators.⁷² (See also Chapter 23.)

In brown coals, the yield of tar appears to be greater for higher water contents at all grain sizes. However, the results are highly dependent on the method of carbonization. Agde and Hubertus believed that during rapid heating of raw coal the surface retains a residue of water to high temperatures, whereas, during slow heating, a dewatering and thermally caused changes of the surface take place before attainment of the higher temperatures. Drying in hot air and steam causes changes by oxidation. Differences in the tar and coke yields may be related not so much to the absolute water content as to the

nature of the heating process by which the water content is reduced.

Thwaites reported an increase in therm value and volume of gas from Australian brown coal containing 61.8 percent water as against the same coal with 12.97 percent water which was attributed to secondary reaction of steam and/or carbon dioxide with carbonaceous matter.

Moisture also has the effect of slowing down the rate of carbonization. Thwaites' experiments indicated the evaporative capacity of a retort to be a constant; hence, the rate of throughput of dry coal will vary inversely as the weight of water in the fuel charged, which is associated with unit weight of dry coal.

Baum believed that water up to 6 percent is without influence on the heat required to carbonize since the heat needed to evaporate the water is withdrawn from the gases given off. Beyond this percentage moisture caused higher fuel consumption, formation of larger quantities of condensation cooling for the gas, and increased volume of ammoniacal liquor to be handled in the manufacture of sulfate of ammonia.

Moisture increases the yield of ammonia, particularly when present during the final stages of carbonization. This has led to the practice of steaming during the carbonization of coal in vertical gas-making retorts.

BRIQUETTING

The critical importance of moisture in the manufacture of brown coal briquets has led to a large amount of study in German laboratories.⁷³

⁷² Thwaite, A. H., *Gas World*, **72**, Coking Sect., 10-1 (1920). Agde, G., and Götz, G., *Braunkohle*, **25**, 1-8, 25-31 (1926-27). Agde, G., and Bendheim, H., *ibid.*, **25**, 721-9, 746-54 (1926-27). Raithe, K., *Braunkohlenarch.*, No. **16**, 1-77 (1927). Sen, B., *Quarterly J. Geol. Mining Met. Soc. India*, **1**, 147-9 (1928). Iki, S., *Ind. Eng. Chem.*, **21**, 239-41 (1928). Dubois, E., *Gas- u. Wasserfach*, **81**, 148-51 (1928). Seidenschneur, F., *Braunkohlenarch.*, No. **25**, 1-16 (1929). Rosin, P., and Just, H., *Braunkohle*, **28**, 893-7, 915-24 (1929). Agde, G., and Hubertus, R., *ibid.*, **31**, 675-80, 877-81, 897-900 (1932). Baum, K., *Gas World*, **98**, Coking Sect. 16 (1933). Farnham, R. V., *Colliery Guardian*, **149**, 1043-5 (1934).

⁷³ Kegel, K., *Braunkohle*, **20**, 161-5 (1921-22), **31**, 253-61 (1932), **38**, 441-50, 461-6 (1939). Terzaghi, K. von, *Erdbaumechanik auf bodenphysikalischer Grundlage*, Deuticke, Leipzig, 1925, 399 pp. Fritzsche, A., *Braunkohlenarch.*, No. **22**, 3-70 (1928); *Braunkohle*, **28**, 873-80 (1929), **29**, 685-95 (1930), **37**, 561-77 (1938). Mayer, M., *Braunkohlenarch.*, No. **28**, 1-72 (1930). Blum, I. L., *Braunkohle*, **30**, 837-40, 853-60

The briquetting of fuels is a process which improves fines obtained through mining and, therefore, is a branch of ore dressing. The addition of special binding materials and the use of heat for drying or softening are not strictly a part of the briquetting process but are additional processes used in conjunction with it. Fundamentally, briquetting is merely an operation in which a press is used to effect the cohesion and compaction of suitable loose fines. Though briquetting appears to be quite simple from a mechanical viewpoint, certain physical factors must be understood in order that the results of the process may be controlled.

Kegel has set down fundamental concepts that concern briquetting. In the first place, all substances are surrounded by a field of attractive force, the strength of which is proportional to the square of the distance between particles. This field of force which surrounds the atom, the molecule, and the colloid is of special importance in connection with the cohesion of particles that are pressed together. According to Kegel, two types of cohesion are possible, true and apparent. In true cohesion, the particles come so close together that the intermolecular binding forces come into full effect. A good example of this type of binding is a salt briquet. Apparent cohesion takes place when wetted particles are pressed so close together that capillary forces are produced; a film on the particles prevents actual contact. Apparent cohesion rather than true co-

hesion is usual in the briquetting of coals. The factors to be considered are the wettability, the closeness of the capillaries, and the surface tension.

There are two types of capillaries: those originally present in the substance, and those formed by pressing the particles together. The second type is effective only when enough liquid is pressed out of the first type to cause effective wetting of the second type. This means that in the absence of a binder the pressure needed for briquetting must be equal to, or greater than, the capillary forces in the first type of capillaries.

Terzaghi, who worked with clays, determined the pressure needed to compress wetter substances to the same extent as they compress themselves through drying. For a formula to evaluate these force relationships and for working methods in this type of procedure, the reader is referred to the original work or to the abstract given by Kegel. It was found that the capillary force of cohesion in clay was greater than one would expect if only the surface tension was responsible. Kegel assumed that this apparent cohesion, since it cannot be accounted for by surface tension alone, is largely augmented by adsorption forces or linkages. He also stated that the viscosity of the wetting medium, usually water, is extremely high in the film since it is under a pressure of several thousand atmospheres, according to his estimate.

Another important consideration, especially in respect to colloidal substances, is that particles with unlike charge, although kept at a certain distance through the action of the film, would be attracted, and particles with like charge would tend to be repelled. Thus, these forces would either add to or lessen the capillary forces.

Since surface tension is one of the important factors in apparent cohesion, the

(1931). Hock, H., *ibid.*, **31**, 559-64 (1932). Hock, H., Fischer, H., and Schrader, O., *ibid.*, **34**, 278-82, 295-98 (1935). Hock, H., and Schrader, O., *ibid.*, **35**, 645-50 (1936); **36**, 781-6 (1937). Sauterlich, K., *Braunkohlenarch.*, No. **48**, 1-21 (1937). Agde, G., and Vetter, K. E., *Braunkohle*, **36**, 813-7 (1937), **37**, 135-8, 421-7 (1938), **38**, 237-40, 255-7, 265-8 (1939). Verlohr, K., *ibid.*, **38**, 145-61 (1939). Vollmaier, E., *Braunkohlenarch.*, No. **49/50**, 30-82 (1938).

presence of a gas phase is essential. If too much liquid is present, the capillaries are extended, the gas phase is removed, and the binding forces are lowered. Fritsche has shown that, in briquetting lignite without a binder, if the pressure is kept the same, there is an optimum water content (see Table IV). At the proper

TABLE IV

EFFECT OF MOISTURE IN THE BRIQUETTING OF LIGNITE, ACCORDING TO FRITSCHÉ ⁷³

Water, percent	5.9	11.7	16.1	33.8
Volume expansion, percent	18.8	17.2	15.9	18.8
Binding strength, kilograms per centimeter	8.0	16.7	18.9	5.5

moisture content the binding strength was a maximum and the volume expansion a minimum. The volume expansion was a measure of the swelling phenomena that followed pressing; it was also a measure of the cohesive forces, which are greatest when they are able to hold the pressed material to a minimum volume.

The wettability of the coal substance is largely dependent upon the rank of coal. In general, the lower the rank of coal, the better the wettability toward water. On the other hand, where binding materials like tar and pitch are used, the wettability toward these substances is in the reverse order; that is, the higher the rank, the better the tar or pitch will wet the coal substance. This explains to a certain degree why substances like lignite can be briquetted with water alone, whereas substances like anthracite require an organic binder. If a substance like lignite is to be briquetted with a tar binder, it must be thoroughly dried in order to make the binder effective.

Some of the general methods that can be used to influence the wettability of coal

substances are as follows: heat, oxidation, reduction, exposure to gas or vapor, and chemical treatment of the surface.

Also a fine, fibrous, hook-type particle is well adapted to briquetting, but a round, hard, coarse type is not.

Another important theory in connection with briquetting has been developed by Blum. He concluded that the amount of free humic acids accompanied by a high water content is a criterion for the briquetting qualities of lignite. Blum's experiments also indicated that carbohydrates and lignin are without influence on the process.

Agde and Vetter have verified Blum's theory, and, though at first they were inclined to believe that the humic acid theory was not in contradiction to the idea that cohesion takes place mainly through the capillary film, later on they said that they doubted the validity of certain of the concepts included in the sticking-film theory. In their latest article, they stated that they now believe that the amount of free humic acid is the controlling factor in the briquetting of lignite.

Kegel in his latest paper considered it possible that the humic acids increase the viscosity of water in the film and, therefore, he did not disagree with the idea that humic acid is important in the briquetting of lignite. He summed up his general conclusions about the briquetting process as follows:

1. The briquetting of loose material through pressure takes place because of a binder, because of wiry matting of fibrous materials, or because of a combination of these factors.

2. When a binder is used the adhesive power of the binding medium toward the material, or the wettability, which tends to oppose or push out the water, is most significant.

3. Hydrophobic, or water-repellent, substances and especially bituminous coals pos-

sess good adhesive qualities toward tar, pitch, and similar substances.

4. The wettability of the material should be only as great as is needed in briquetting so that the intermolecular forces will be strong enough in proportion to the wetting properties to avoid the disturbing swelling phenomena.

5. In regard to the binding forces of a hydrophilic material, the wettability can be lowered, and the intermolecular forces can be raised, by suitable means. The lowering of the wettability can be accomplished through treatment with gas, through aging, through drying at a high temperature if necessary until a water content of zero percent is reached, and through the prolonging of the action of heat. A raising of the intermolecu-

lar forces may be brought about by using fine particles, by increasing the plasticity, or by avoiding any treatment of the material that causes a resistance to change of form.

SUMMARY

The moisture content is an important factor in the storage and utilization of coals. In the lower-rank, high-moisture coals it affects slacking or weathering and is a critical variable in briquetting. In the carbonization of bituminous coals its importance is related chiefly to the bulk density. Tempering coal with water may affect combustion favorably.

CHAPTER 18

CHANGES IN COAL DURING STORAGE *

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Significant changes in the physical and chemical properties of coal occur upon exposure to air at atmospheric temperatures. Ordinarily these changes take place slowly but continuously from the moment the face of the coal bed is exposed to air until the coal is finally utilized, causing a gradual decrease in commercial value.

Normally the largest part of this weathering occurs in the storage pile. About 36 million tons of bituminous coal was kept in storage in 1939. This amounted to an average supply sufficient for 35 days' operation of the plants for which the coal was destined.¹ Judging by the period of heightened national effort in 1918,² the amount of coal in storage would be expected to increase during World War II, and did actually reach over 70 million tons in July, 1942.

Barring emergencies caused by interruptions in supply or by spontaneous ignition, the length of time that coal is left in a stockpile is determined by the management upon the basis of balancing cost of

storage and recovery against the extent of deterioration of the coal. A large number of piles remain undisturbed for many years. Storage for six to eight months is common practice at plants that find it advantageous to obtain coal via water routes that are closed during the winter. In this connection, it is interesting to note that over 46 million tons of bituminous coal was loaded into vessels at Lake Erie ports in 1940, a new record.³

Weathering of coal in storage is particularly important to operators of coke ovens because continuous operation is imperative and consequently large stocks must be kept on hand to allow for possible interruptions in supply. Furthermore, the coking power of coal can be destroyed completely by storage in air for a long time, and even overwinter storage may result in coal that must be mixed with fresh coal before coking.

The gradual changes that take place in coal on exposure to air are accelerated greatly if the temperature of the coal pile rises; the more spectacular phenomenon of spontaneous ignition may occur. Little information is available on the annual economic losses due to spontaneous ignition in

* Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

¹ McMillan, M. E., Anderson, R. L., and Young, W. H., *Minerals Yearbook, Review of 1939*, U. S. Bur. Mines, 1940, p. 802.

² Stoek, H. H., Hippard, C. W., and Langtry, W. D., *Univ. Illinois Eng. Expt. Sta. Bull.*, **116** (1920), 157 pp.

³ U. S. Bituminous Coal Division, *Monthly Coal Distribution Reports*. Voskuil, W. H., and Oliver, G. N., *Illinois State Geol. Survey Rept. Investigations* **74**, 16 (1941).

mines or in coal-storage piles. However, these losses are probably of considerable magnitude if one judges by the insurance rates, which have been reported to be as high as 3 percent of the value of a storage pile,⁴ and by the large amount of money invested in coal in storage. Any improvement in methods of storage or of compensating for the changes that occur in storage that may result from studies of the problem should result in very considerable economic gains because of: (1) decreased losses in storage and (2) improved plant efficiencies from better quality of coal or greater uniformity.

From the scientific standpoint, study of the rate of oxidation of coal is particularly interesting because the reaction proceeds slowly enough under ordinary conditions so that accurate measurements can be made on the effect of each of the various factors that control its rate. The results of these investigations are of general interest in studies of kinetics of heterogeneous chemical reactions and also have some bearing on combustion studies. All laboratory tests on coal, no matter what their purpose, are necessarily made upon samples which have had some previous weathering experience, so that in interpreting the experimental data obtained some estimate must always be made as to the extent and importance of any changes caused by adventitious weathering.

Qualitatively, the general changes that take place in coal on storage (barring serious spontaneous heating) are increases in weight, oxygen content, hygroscopicity, ignition temperature, and solubility in caustic solutions and in alcohol and decreases in carbon and hydrogen content, heating value, coking power, and average particle size.

The extent of these changes depends on the duration of exposure to air and the rate of the oxidation reaction. The rate of the oxidation reaction under the various conditions of storage is therefore of sufficient importance to be worthy of detailed study. Furthermore, the question whether or not spontaneous ignition will occur in a given storage pile is determined entirely by the rate of oxidation and the rate of heat loss from the pile.

The major changes when broken coal is exposed to air (for example, in storage above ground) are: (1) changes caused by interaction of the coal with the oxygen in the air and (2) changes in moisture content that may result in appreciable slacking or size degradation. The changes caused by interaction with oxygen often are evidenced by lowered heating value and changed combustion characteristics, impairment of coking properties, or spontaneous combustion. Slacking, friability, and size degradation on storage will be discussed later.

Even though a lump of coal is cold to the touch it is uniting with the oxygen of the air at a measurable rate and will continue to do so for a great many years. The gaseous products given off by this low-temperature "combustion" are the same as when the coal is burned at high temperature in the furnace, namely, carbon dioxide, carbon monoxide, and water. The greatest difference between these high- and low-temperature oxidations lies in the lower rate at low temperatures and in the fact that at low temperatures about half of the oxygen consumed remains upon the coal, often causing the coal to gain in weight instead of wasting away.

As will be shown later, this low-temperature oxidation reaction is highly exothermic; moreover, the rate of reaction increases very rapidly with increasing tem-

⁴ Abbott, W. L., *Power Plant Eng.*, **33**, 44 (1929).

OBSERVATIONS ON STORAGE PILES

perature. These two facts account for the often-observed phenomenon of spontaneous ignition in coal piles, which has also been observed in a large variety of other materials, such as soap chips,⁵ powdered metals, hay, and grains. These two factors that are conducive to spontaneous ignition tend to be compensated by a rapid decrease in rate of oxidation with time of oxidation or, what amounts to the same thing, with extent of oxidation, or the amount of oxygen already consumed. As a result of this compensating factor it is very difficult to prophesy whether a given pile will ignite spontaneously. However, whether or not a coal pile shows a serious temperature rise, oxidation proceeds, and progressive changes in combustion properties and in coking properties, and loss in heating, are inescapable as long as the coal remains in contact with the oxygen of the air.

OBSERVATIONS ON STORAGE PILES

Actual observation of large storage piles, with proper testing of coal, etc., is, of course, the most direct method for ascertaining the changes that take place in coal on storage. This method is subject to the disadvantage that, because of lack of control of conditions, duplicate results on seemingly similar piles are rarely obtained, and so a large number of piles must be investigated if reliable data are to be obtained. Nevertheless, much valuable information has been obtained by studies of large storage piles; in fact, much of the laboratory work done under closely controlled conditions has for its aim the explanation and correlation of the facts found by these studies of large piles.

⁵ Freitag, *Zentr. Gewerbehyg. Unfallverhüt.*, **21**, No. 1-2, 15-6 (1934); *Chimie & industrie*, **32**, 578 (1934). Chataway, H. D., *J. Soc. Chem. Ind.*, **47**, 167-71 (1928).

In 1879, Fayol⁶ recorded the temperatures in various parts of a special large pile of Commentry coal. The coal was piled at a temperature of 22° C, and after 90 days a maximum temperature of 150° C was recorded at a point 1 foot from the ground in a part of the pile that was 20 feet deep. In another test he showed that the temperature of a pile of coal that was heating could be caused to fall by merely excluding air with a tight cover. His results showed that spontaneous ignition did not occur in piles less than 6 feet deep.

In 1909, Threlfall⁷ filled two 250-ton bins with coal containing 0.5 percent sulfur, and kept both bins under identical conditions, except that the coal in one bin was thoroughly wetted and permitted to drain free of excess water. The temperature in the dry bin rose gradually at first and then more rapidly until at the end of ten weeks it reached 135° C. The coal was kept from firing only by digging out. The wet coal did not rise to 50° C.

In 1908, Erdmann and Stoltzenberg⁸ believed ozone to be responsible for the spontaneous firing of coal. They noted that fires occurred more frequently on warm, sunny days after a rain when conditions were ideal for the formation of ozone. Laboratory tests proved that humic acid obtained by extraction of coal with alkali was very reactive to ozone. Briquetted coals reacted less vigorously, but iron pyrites did not react if dry, and only slightly if moist.

Parr⁹ stored 25-ton samples of three Illinois coals for six years, keeping a good

⁶ Fayol, H., *Bull. soc. ind. minérale*, (2), **8**, 487-746 (1879).

⁷ Threlfall, R., *J. Soc. Chem. Ind.*, **28**, 759-72 (1909).

⁸ Erdmann, E., and Stoltzenberg, H., *Braunkohle*, **7**, 69-73 (1908).

⁹ Parr, S. W., *Univ. Illinois Eng. Expt. Sta., Bull.* **97** (1917), 44 pp. Parr, S. W., and Wheeler, W. F., *ibid.*, **38** (1909), 43 pp.

record of the change in screen analysis and in the heating value. Whether the coal was stored in the open or in closed bins the results indicated about the same amount of degradation in size and about the same loss in heating value. The average increase in fine coal (through $\frac{1}{4}$ inch) caused by weathering for one and a half years was 13.3 percent of the original amount of coarse coal (on $\frac{1}{4}$ inch). In six years this value increased to 22 percent.

The heating value of the coal decreased by about 6 percent (moisture- and mineral-matter-free basis) in six years. Boiler tests¹⁰ made using the coal weathered for six years showed that the weathered coal required a thinner fire and more draft and proved somewhat more difficult to ignite. However, with correct handling, overall boiler and grate efficiencies were as high with weathered as with fresh coal.

As the result of an extensive series of experiments and observations, Parr summarized the factors to be considered in the storage of coal to avoid the approach to those dangerous temperatures that lead inevitably to ignition of the mass:

1. Segregation of sizes in piling results in coarse-sized areas or portions serving as ducts for conducting air through the pile and so invites local heating in areas where fine sizes are located. The piling of screenings in such a way as to create channels for the free passage of air, as by coning with consequent rolling down the side of nut sizes, will insure heating at the margins of the chimney thus formed. Posts, girders, or braces may afford ready access of air and promote heating at such points. Screenings can be successfully stored if conditions are maintained that prevent circulation of air, and coarse sizes store well if fines are absent.

2. The height of piles is limited by the increased tendency toward segregation of sizes with increase of height. In piles of moderate height (10 to 15 feet), there is the added advantage of dissipating the heat by conduction and radiation, as well as the possibility of quick removal of hot spots for use under the boilers.

3. The question of coal type is relatively unimportant compared to the conditions of storage.

4. Coal in storage, which has acquired a temperature of, say, 75° C, will proceed to the point of ignition unless conditions are altered.

Porter and Ovitz¹¹ reported observations on 350-pound samples of Sewell Seam (West Virginia) coal crushed to pass a $\frac{1}{4}$ -inch screen that were exposed to the weather in various parts of the country for periods of time up to five years. Samples were taken periodically for analysis and determination of heating value. The maximum deterioration in heating value in one year was 1.2 percent in $\frac{1}{4}$ -inch coal exposed indoors at Key West; and the maximum in two years was 2.1 percent in the same portion after a second year out-of-doors. Exposure in the more moderate climates of Pennsylvania, New Hampshire, and Virginia resulted in losses in heating value of about 1.5 percent for five years' exposure. With this coal, no significant difference was found between complete exposure and exposure under a roof. Run-of-mine coal stored under the same conditions showed only 50 to 75 percent as great a loss in heating value as the crushed coal. Coal submerged in water showed no significant loss in heating value. Any indications of change in percentage oxygen and percentage sulfur in the coal during outdoor storage were within the experimental

¹⁰ Kratz, A. P., *Univ. Illinois Eng. Expt. Sta., Bull.* 78 (1915), pp. 48-52.

¹¹ Porter, H. C., and Ovitz, F. K., *U. S. Bur. Mines, Bull.* 136 (1917), 34 pp.

error of their determination. Similar tests on 3-ton lots of Pittsburgh Seam coal (Pennsylvania) exposed in open bins for five years showed losses of less than 1.1 percent in heating value in five years.

Tests initiated in 1907 on 3- or 4-ton lots of Sheridan (Wyoming) subbituminous coal (22 percent bed moisture) stored for $2\frac{3}{4}$ years in five bins, one of which was without cover, resulted in losses of 3.2 to 5.3 percent in heating value when no allowance was made for the probable increase in weight due to oxidation. Coal piled 5 feet deep, in a bin without cover, showed the lowest loss in heating value (3.2 percent) because of the formation of a 12-inch layer of fine slack on top that helped to protect the lower layers from oxidation and drying. The authors recommended bins with air-tight bottoms and sides of concrete for storage of coals of this type. In $2\frac{3}{4}$ years, the moisture content of the coal in the covered bins decreased on the average from 21 to 15 percent. The moisture loss (from 21.4 to 12.5 percent) and also the loss in heating value (5.3 percent) was greatest in the bin where the coal was piled deepest (15 feet), but there were no other indications that the coal had heated in storage. Preliminary moistening of the coal had no significant effect on deterioration of the coal in storage. Screenings stored about as well as run-of-mine. The sulfur content decreased from 1.61 percent (dry, ash-free basis) to 1.17 percent. The ash content on a dry basis was 10.8 percent initially compared to a final value of 11.1 percent.

Observations¹² on Sydney coal in a 58,000-ton pile (15 feet high) near Montreal, Canada, which was piled between June and October, 1910, showed that a

temperature of 55° C was reached in the middle of the pile on the following February 15; when the pile was ventilated by driving in 2-inch bars and withdrawing them, the temperature fell and danger of fire was averted (the outside air temperature was about -13° C). A gas analysis of the air from the zone at 55° C showed about 17 percent oxygen and 0.5 percent carbon dioxide. A foot or two of snow covered the pile, even when this temperature of 55° C prevailed 6 feet from the top of the pile. Measurements of air currents and pressures indicated that the flow of air through the pile was small and very difficult to measure.

Experiments were made in 1911 on Phalen Seam coal at Glace Bay, Nova Scotia, on 90-ton piles. One pile, 16 feet high, of fresh run-of-mine coal showed a maximum temperature of 38° C, 44 days after piling, 3 or 4 feet under the surface of the pile. A sample of air was taken from a point about 10 feet from the surface of the pile and 5 feet from the ground. The temperature of the coal at this point was 35° C. Analysis of the air sample showed 20.4 percent oxygen instead of the normal value of 20.93 percent. Apparently under these conditions there was an ample supply of oxygen at all parts of the pile.

Stoek, Hippard, and Langtry² sent out about 18,000 questionnaires to manufacturing plants, coke plants, power stations, etc., requesting information on coal-storage practice and experience with spontaneous ignition. They received more than 300 answers, and in addition they investigated personally other examples of fires in storage piles. About 75 percent of the fires in coal piles that were studied occurred within 90 days after the coal was placed in storage. The authors concluded that the weight of evidence in the United States seemed to be against the practice of venti-

¹² Porter, J. B., et al., *An Investigation of the Coals of Canada*, Vol. 7, Government Printing Bureau, Ottawa, 1915, 188 pp.

lating coal piles. The place of storage should preferably have a hard, level, clay bottom, naturally drained, or else drains should be provided about the storage pile, not underneath it, as a drain beneath a pile may produce an air current up through the pile and thus assist spontaneous combustion. It is wise to select low-sulfur coals for storage, if obtainable, but it must not be taken for granted that a low-sulfur coal will necessarily store well. Coal should either be so piled that air may circulate freely through it and thus carry off any heat generated or else be so closely packed that air cannot enter the pile. Water should be used for putting out a fire in a coal pile only as a last resort after other means, such as moving the coal, have been tried to lower the temperature. Coal that has once heated should preferably be used at once and not be returned to the pile.

Seymour¹³ made observations on a coke-oven plant on the Great Lakes that stocked its entire coal supply for six months each year. There was definite correlation between the extent of oxidation of the coal and the coke required per ton of iron from the blast furnaces. Extent of oxidation was measured by time in storage, increased solubility in caustic solution, and the characteristics of the coke buttons formed in the determination of volatile-matter content. The yields of byproducts also varied with the extent of oxidation of the coal.

In 1928, Hoskin¹⁴ made a survey of the practical experience available on storage of Indiana coal. A very small percentage of the coal piles investigated exhibited spontaneous ignition. Most fires that did develop were found in the first three months of storage. Extraneous materials, such as

wood, caused some fires. Moisture conditions, rain, etc., were related intimately to the occurrence of fires. In one instance coal that was loaded on wet ground with some puddles of water fired quickly for no other observable reason; in another, a pile of old, dried screenings that had been stored indoors for a long time was used as a base for new screenings, and thirteen days later fire was discovered along the plane of contact of the two coals. One successful method of storage was to compact the piles by rolling during the piling operation. The bulk density of 2-inch Indiana screenings was increased by 24 percent by rolling, indicating an expulsion of the greater part of the air originally in the screenings.

In 1929, Graham and Raybould¹⁵ stored 15 tons of fine coal (80 percent through 4 mesh) in a boiler bunker and sealed off the top with boards and a layer of clay. The walls apparently were airtight, except for an opening 4 feet by 5 feet closed with loose boards. A stack equipped with a damper was connected at the top of the pile to regulate and measure the rate of air flow. Tubes were inserted in the coal to withdraw samples of gas for analysis. In five weeks the average temperature of the bin rose from 70° to 120° F. The average percentage oxygen in the air in the bin was about 1 percent. Twenty-five percent of the oxygen consumed went to carbon dioxide and 1 percent to carbon monoxide. At five points in the lower half of the bin, where the average temperature was 140° F, the percentage of oxygen in the air rarely exceeded 0.5 during three or four months. Early in the experiment the point of highest temperature was about 2 feet from the floor, but after 20 weeks the point of highest temperature was 6 feet from the floor

¹³ Seymour, W., *Blast Furnace Steel Plant*, 9, 435-7 (1921).

¹⁴ Hoskin, A. J., *Purdue Univ. Expt. Sta., Bull.* 30 (1928), 61 pp.; *Black Diamond*, 80, No. 14, 12-3 (1928).

¹⁵ Graham, J. I., and Raybould, W. E., *Trans. Inst. Mining Engrs.*, 83, 89-101 (1932).

or 3 feet from the top. After 2½ months, at a point 3 feet from the floor, where the coal temperature was 140° F, a gas analysis showed an oxygen content of zero percent. When the oxygen content was raised to 3.4 percent by allowing more draft, the temperature at this point increased rapidly.

Dunningham and Grumell,¹⁶ in experiments on large piles of Midlands coal, showed that ventilation with wooden ducts installed before the coal was piled decreased the likelihood of spontaneous heating more than rolling or packing. Placement of the ducts near the periphery of the pile proved sufficient. The tests indicated that, in piles of fresh coal over 8 feet high, segregation and exposure to wind should be avoided. The piles ventilated by ducts showed little deterioration in calorific value, size, or coking power after 3½ years' storage. Four or five years in the pile lowered the heating value by about 0.5 percent where no heating had occurred. Similar piles without duct ventilation, whether or not rolled, showed considerable reduction in coking power after two years.

The principle of exclusion of air from coal piles is well illustrated in a series of tests by Drewry.¹⁷ Pile 1 was 50 feet high and contained 120,000 tons of dusty, run-of-mine coal of 2.83 percent sulfur content. It was carefully packed to 18 percent greater than usual density, but heating started within two months. The top was leveled and coated with asphalt to neutralize the stack effect, but heating continued until one point reached 800° F. The sides were then covered with a 4-inch layer of 5/16-inch screenings and a 1/8-inch coat of asphalt. The "hot spot" temperature fell quickly from 800 to 400° F, and

the maximum temperature in the pile fell slowly through about 14 months to a winter equilibrium temperature of 165° F. Gases under the asphalt cover showed contents of oxygen as low as 1.6 percent. The coal was removed during an eight-month period without trouble. The asphalt covering pulverized and burned satisfactorily. The cost of the complete asphalt coating was about 1 percent of the coal cost. The heat loss for the three years' storage was 4.15 percent. Pile 2 was also 50 feet high and contained 40,000 tons of coal of 1.5 percent sulfur content. This pile was leveled, smoothed, and coated, top and sides, with a 12-inch layer of "-48 mesh" dusty coal; over this was placed a 12-inch layer of large screenings to pack it and prevent wind and water erosion. The maximum temperature observed in the center of the pile was 86°, and the hottest spot found was 165° F. The cost of the fireproofing by this method was 2/3 percent of the cost of the coal, and the heat loss on 1½ years' storage was negligible. Pile 3 contained 45,000 tons of coal and had no fireproofing. It caused much trouble from overheating and required considerable rehandling and the removal of the hottest spots six months after storage. The net heat loss in nine months was 1 percent. Pile 4 contained 75,000 tons of coal and was covered similarly to pile 2, with satisfactory results.

Covering a large coal pile with a layer of very fine coal and then with a layer of lump coal forms an efficient, airtight coating that inhibits spontaneous heating, reduces heat losses from storage, and has become standard practice with some companies whenever coal must be stored nine months or longer. Some solar heating may be expected, and occasional air leaks have to be stopped for the best storage results.

In connection with exclusion of oxygen from coal piles it should be mentioned that

¹⁶ Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel*, 10, 170-7 (1936).

¹⁷ Drewry, M. K., *Combustion*, 8, No. 8, 28-32 (1937).

Olin found that a mixture of 1.5 pounds of aluminum sulfate and calcium carbonate per ton of coal decreased the tendency of Iowa coal to heat spontaneously.¹⁸

The preceding abstracts of observations on large piles of coal are typical, but many other valuable reports have been made covering large-scale studies of deterioration in storage,¹⁹ and especially the spectacular and sometimes mysterious phase of this study, spontaneous ignition.²⁰ Reviews on this subject were prepared by Davis and Reynolds²¹ and Hoskin¹⁴ in 1928 and by Porter¹² in 1915. Many writers have given recommendations for improved storage practice.^{22, 23}

Both deterioration and spontaneous ignition can be avoided by under-water storage. At least one American plant has facilities for storing as much as 300,000 tons under water.²⁴ Both the rate of deterioration and the probability of spontaneous ignition can be decreased by storing coal in compacted layers. Coal can be laid

down in 2- to 4-foot layers by spreading with a caterpillar tractor shoving a bulldozer and hauling a carryall.²⁵ The bulk density of broken coal can be increased from 45 to 50 pounds per cubic foot for loosely piled coal to 65 pounds per cubic foot by compacting.²⁶ This method of compacting violates the old precept that the production of fines should be avoided.²⁷ The success of the method seems to indicate that the decreased availability of oxygen through decreased air circulation²⁸ more than compensates for the increased area of fresh coal surfaces caused by breakage. Surprisingly little information has been published on the important factor of availability of oxygen in storage piles, that is, the percentage of oxygen in air within the piles. The principle of decreased air circulation has been further applied in the use of a layer of paper between layers of coal. This method has proved successful where it was necessary to store a coal that was especially sensitive to oxidation.²⁹

In connection with fines it should be mentioned that in some plants it has been found practicable to screen out fines before storage, and the resultant fuel is not subject to spontaneous ignition.³⁰

Apparently no application has been reported of the very interesting principle of decreasing voids in coal piles by the method described by Furnas.³¹ This method of layered storage makes it possible to obtain

¹⁸ Olin, H. L., *Fuel*, **16**, 256-8 (1937).

¹⁹ Bement, A., *Trans. Am. Inst. Chem. Engrs.*, **3**, 281-6 (1910). American Engineering Council, *Industrial Coal: Purchase, Delivery and Storage*, Ronald Press Co., New York, 1924, 419 pp. Voitova, E. V., and Zamyatina, L. A., *Coke and Chem. (U.S.S.R.)*, No. 2-3, 29-39 (1936); *Chem. Abs.*, **31**, 1582. Rammner, E., *Braunkohle*, **38**, 659-61, 667-70 (1939).

²⁰ Anderson, J. H., *Trans. Inst. Marine Engrs.*, **30**, 81-98, 98-120 (1918). Scully, T., *Can. Mining Met. Bull.*, **231**, 808-15 (1931), **235**, 1310-7 (1931). Jaeschke, A., *Glashütte*, **64**, 515-8 (1934). Bielenberg, W., *Angew. Chem.*, **48**, 779-81 (1935).

²¹ Davis, J. D., and Reynolds, D. A., *U. S. Bur. Mines, Tech. Paper* **409** (1928), 74 pp.

²² Potter, A. A., and Solberg, H. L., *Power*, **68**, 344-5 (1928). Kammerer, V., *J. usines gaz*, **55**, 152-4 (1931). Andrews, D., *Steam Engr.*, **3**, No. 9, 370-2 (1934). Hantke, G., *Przemysl Chem.*, **22**, 360-7 (1938). Fuchs, P., *Arch. Wärmewirt.*, **21**, 39-41 (1940).

²³ Blanke, M., *ibid.*, **16**, 97-9 (1935); *Gas- u. Wasserfach*, **79**, 13-4 (1936).

²⁴ Abbott, W. L., *Power Plant Eng.*, **33**, 44-5 (1929).

²⁵ Dow Chemical Company, *Black Diamond*, **104**, No. 6, 13-4 (1940).

²⁶ Lindseth, E. L., and Leonhard, F. J., *Combustion*, **7**, No. 3, 19 (1935).

²⁷ Stoek, H. H., *U. S. Bur. Mines, Rept. Investigations* **2109** (1920), 8 pp.

²⁸ Tuttle, M. A., *Power*, **69**, 271 (1929). Wehrmann, O. O., *Gas- u. Wasserfach*, **73**, 144-6 (1930).

²⁹ Brown, W. T., *U. S. Pat.* 2,251,321 (1941).

³⁰ Brauer-Angott, H., *Braunkohle*, **37**, 169 (1938).

³¹ Furnas, C. C., *U. S. Bur. Mines, Rept. Investigations* **2894** (1928), 10 pp.

large increases in bulk density (decreased voids) without breakage of coal by exercising some control of the screen sizes going to a layer.

However coal is stored, it is apparent that if serious rises in temperature do not occur the loss in heating value seldom is large enough to have great commercial importance. For example, samples of coal ($\frac{1}{2}$ to $\frac{1}{16}$ inch) in wire mesh containers buried in 8-ton storage piles showed a decrease in heating value of about 1.26 percent in $2\frac{1}{2}$ years.³² In another pile, ten years' storage caused a loss of less than 5 percent in the total amount of available heat.³³ An average annual loss in heating value as low as 0.11 percent has been reported for coking coals stored in large piles.¹⁶

The same cannot be said for loss in coking power. With some coals, the loss in coking power is said to be so rapid that storage for as short a time as 48 hours has a serious effect.³⁴ Actual storage tests on weakly coking coals show that the coking power is affected before there is any appreciable change in other properties.³⁵ Illinois coals, for example, should be coked within two weeks after removal from the mine face.³⁶ The coking power of some coals, however, is not affected seriously by four years of ordinary storage or ten years of storage under special conditions.³⁷

The conclusions and recommendations of the many writers on the subject of storage and spontaneous ignition can be summarized as follows:

³² Scarf, F., Hall, D. A., and Yearsley, C. W., *Trans. Inst. Mining Engrs.*, **100**, 88-129 (1941).

³³ Mackay, H. F., *J. Inst. Engrs., Australia*, **11**, 290 (1939); *Fuel*, **19**, 4 (1940).

³⁴ Davies, D. T., and Wilkins, E. T., *Yearbook Coke Oven Manager's Assoc.*, **1939**, pp. 218-9.

³⁵ Jamieson, J., and Skilling, W. J., *Gas World*, **110**, 301-7, 324-30 (1939).

³⁶ Thiessen, G., *Illinois State Geol. Survey, Bull.* **64** (1937), p. 206.

³⁷ Hogg, J. C., *Gas J.*, **230**, 440-1 (1940).

1. Storage area should be level, firm, well drained, and free of fences, piers, etc.

2. Decreased height of storage piles results in decreased probability of spontaneous ignition,³⁸ since (a) the effective resistance to heat flow is lower, so that the heat of oxidation can be dissipated with less rise in temperature, (b) lower piles tend to decrease the amount of segregation of sizes when coal is piled carelessly, and (c) it is easier to remove "hot spots" when they occur.

3. Segregation of sizes should be avoided since many fires occur near the boundaries of zones of coarse coal that apparently act as chimneys for conducting air into the pile.³⁹

4. Preferably coal should not be piled in hot weather⁴⁰ since many fires apparently are due to this cause.

5. Coals from different sources should not be stored in a common pile.^{23, 41}

6. A shipment of coal that is especially wet should not be piled with other coal.^{14, 40, 41}

7. Care should be taken to keep out extraneous material, which may cause fires, even in anthracite, which is not ordinarily subject to spontaneous ignition.⁴²

8. After storage the temperature of a pile should be determined regularly by means of thermometers in previously installed pipes or by thrusting down iron rods and feeling the rods on withdrawal. The extremely local nature of "hot spots" makes it necessary to test at points on 10- to 20-foot centers; if temperatures of 140

³⁸ Editorial, *Gas J.*, **199**, 199-201 (1932).

³⁹ Hudler, J., *Brennstoff- u. Wärmewirt.*, **10**, 419-21 (1928).

⁴⁰ Ward, A. T., *Blast Furnace Steel Plant*, **17**, 298-301 (1929).

⁴¹ *Maryland Bur. Mines, Monthly Notes*, November, 1937.

⁴² Jones, G. W., and Scott, G. S., *U. S. Bur. Mines, Rept. Investigations* **3468** (1939), 13 pp.

to 150° F are found, danger is impending,⁴³ and the temperature of the coal near these points should be taken on 5-foot centers; ²⁶ even so, it is possible to miss "hot spots," and combustible gas indicators have been used successfully for their detection.⁴⁴

9. If coal at a temperature above 150° F is found it should be dug out and used immediately or wet down thoroughly and re-piled by itself. Water should be sprayed on the large piles only as a last resort.¹⁴

10. The following heights of storage piles are recommended as safe: ²³ fine coal over 18 percent volatile matter, up to 4 yards; large coal over 18 percent volatile matter, up to 6 yards; fine coal below 18 percent volatile matter, up to 6 yards; and large coal below 18 percent volatile matter, up to 8 yards.

STUDIES OF RATE OF THE OXIDATION REACTION UNDER CONTROLLED CONDITIONS

Knowledge of the kinetics and mechanism of the oxidation reaction is an excellent guide both to better storage practice and to better methods of compensating for the changes in stored coal. This knowledge can be obtained by laboratory studies under closely controlled conditions where each condition can be varied separately and its effect on rate determined. Aside from the immediate practical value of such experiments considerable light is thrown upon the constitution of coal.

RATE OF ATMOSPHERIC OXIDATION AT CONSTANT TEMPERATURE

The following experimental method can produce results of considerable accuracy, and the results can be given wide interpretation because all conditions can be put

under precise control. A sample of crushed coal is maintained at constant temperature and exposed to air flowing at a measured rate through the coal. The oxygen in the air combines with the coal, and the rate of disappearance of oxygen can be measured accurately by gas analysis of the effluent air. The amount of gaseous oxygen (O₂) that disappears from the gas phase in a given time (that is, the amount of oxygen consumed) is then used as the measure of the rate of the oxidation reaction. In other words, oxygen consumed equals the oxygen in the gaseous products immediately evolved (carbon monoxide, carbon dioxide, and water) plus the oxygen remaining upon the coal. The extent of oxidation of a sample is measured by the amount of oxygen that has been consumed. The results of many experiments obtained under conditions similar to those outlined above have been reported in the literature.

Wherever a sample of fresh, unoxidized coal is used the rate of oxidation decreases very rapidly with time at first and then finally approaches a more nearly constant value. Formerly, this large change in rate with time of oxidation or with extent of oxidation made it difficult to compare the results of different experiments or to use the results to characterize a given coal. Even the calculated average rate of oxidation of a coal depends entirely on how long the particular experiment was continued. Work at the U. S. Bureau of Mines⁴⁵ has shown that rather simple and apparently general relationships exist between rate of oxidation and time or extent of oxidation. Use of these relationships aids greatly in all studies of the reaction.

It was found that the course of the oxidation reaction could be described very ac-

⁴³ Hood, O. P., *U. S. Bur. Mines, Circ.* **7074** (1939), 5 pp.

⁴⁴ Campau, G. F., *Combustion*, **9**, No. 10, 30 (1938).

⁴⁵ Schmidt, L. D., and Elder, J. L., *Ind. Eng.*, **32**, 249-56 (1940).

curately by means of the following general equation:

$$X = Ct^b \quad (1)$$

where X = amount of oxygen consumed, expressed as grams of oxygen per 100 grams of the original fresh coal, moisture- and mineral-matter-free basis, or, in short, percentage by weight of the unoxidized pure coal; t = days in oxidation apparatus; C = a constant, the value of which equals the amount of oxygen (percent by weight of pure coal) that reacts with the coal sample in the first day under the experimental conditions used; and b = a constant, the value of which apparently is about the same for all coals of the same particle size. The physical meaning of equation 1 can be stated simply: at any stage in the isothermal oxidation of a coal sample, a 1 percent increase in time of oxidation will increase the extent of oxidation X by b percent.

As will be seen later, the values of b for the samples investigated ranged from 0.37 for minus 200-mesh samples to 0.8 for 0- to $\frac{1}{4}$ -inch coal.

Differentiating equation 1 with respect to time:

$$\frac{dX}{dt} = bCt^{b-1} \quad (2)$$

For convenience of notation let $dX/dt = R$; then

$$R = bCt^{b-1} \quad (3)$$

equals rate of oxygen consumption, percent by weight of pure coal per day.

If data obeying the relation shown by equation 3 are plotted on log-log scales, the points fall along a straight line. As will be shown, this equation can be used to check observed results when experimental conditions are such that the rates of oxidation are measured directly after successive intervals of time of oxidation.

Winmill and Graham,⁴⁶ working at the Doncaster Coal Owners' Research Laboratory with J. S. Haldane, have reported the results of an extensive series of experiments which were well thought out and were executed in an especially thorough and careful manner. In these experiments, 150-gram samples of coal, crushed to pass a 200-mesh screen, were oxidized at constant temperatures in a stream of moist air that passed through the crushed coal at measured rates. Analyses of the effluent air from time to time gave the momentary rates of oxygen consumption. The investigators reported rates of oxidation as cubic centimeters of oxygen (N.T.P.) consumed per 100 grams of coal (as received) per hour. The results of one typical series of experiments on "Jacks" coal (through 200-mesh screen) from the Barnsley Seam are shown plotted on log-log scale in Fig. 1.

The experimental points fall very closely along straight lines, which is excellent confirmation that the general relationship (equation 3) correctly correlates rate of oxidation with time of oxidation.⁴⁷ The values of b , calculated from the slopes of the straight lines, and the quantities C , evaluated from the intercepts and converted to the appropriate units, are shown in Tables I and II.

The fact that the straight lines in Fig. 1 are all very nearly parallel (constant value of b), regardless of the temperature of ox-

⁴⁶ Winmill, T. F., *Trans. Inst. Mining Engrs.*, **46**, 563-78 (1913-14), **48**, 503-20, 535-49 (1914-15), **51**, 493-9, 510-47 (1915-16). Graham, J. I., *ibid.*, **48**, 521-34 (1914-15), **49**, 35-43 (1914-15). Thomas, W. M., Jones, T. D., and Graham, J. I., *Proc. S. Wales Inst. Engrs.*, **49**, 201-36, 305-7 (1933).

⁴⁷ The results of over 80 test series on various coals tested in several types of apparatus have been subjected to this method of analysis. In each series equations 1 and 3 correlate the data very satisfactorily.

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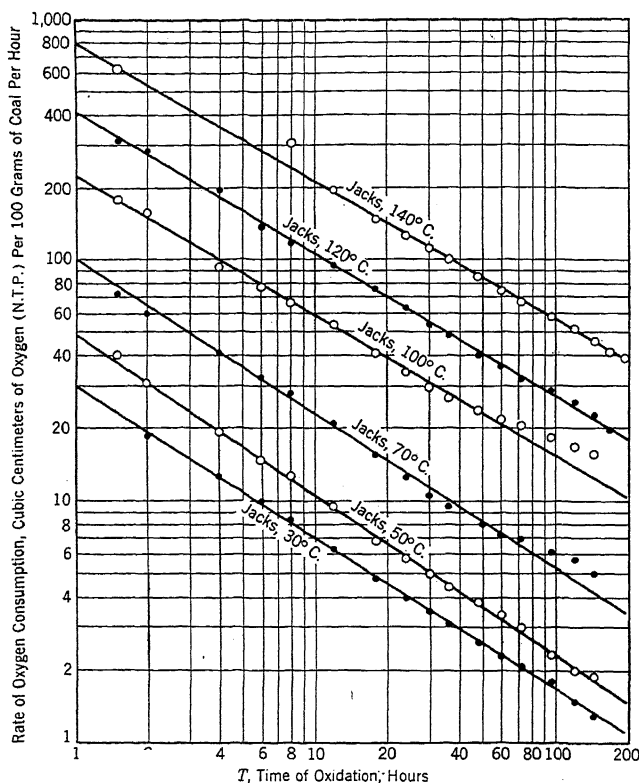
FIG. 1. Change of rate of oxygen consumption with time for "Jacks" coal from the Barnsley Seam.⁴⁶

TABLE I

VALUES OF THE EXPONENT b FOR SIX COALS (-200-MESH) AT VARIOUS TEMPERATURES

Temperature, °C	30	40	50	70	80	100	120	140	160	Aver.
Hards	0.373	0.363	0.305	0.333	0.328	0.368	0.376	0.343	0.237 *	0.349
Jacks	.372343	.362426	.416	.429392
Cannel	.364386	.411429	.425	.434408
Barnsley Softs	.367312	.278351	.343	.387340
Top Softs323	.367422	.403	.402384
Shale	.389364	.361203 *371
Average	.373	.363	.339	.352	.328	.367	.393	.399372

* Excluded from average.

dation, is a striking illustration of the fact that rates of oxidation decrease with time in almost exactly the same manner, regardless of how fast the coal oxidizes under the

particular experimental conditions. The value of b is essentially the same for different coals⁴⁵ and depends primarily on particle size.

Combining equations 1 and 3:

$$R = \frac{bC^{1/b}}{X^{(1/b)-1}} \quad (4)$$

This equation shows quantitatively the decrease in rate of oxidation with increasing extent of oxidation. The rate varies inversely with X raised to a power which ranges from 0.25 for 0- to $\frac{1}{4}$ -coal⁴⁵ to 1.7 for 200-mesh coal ($b = 0.37$).

In Fig. 2, typical curves are shown for both fine and coarse coals, illustrating the decrease in rate and the increase in extent of oxidation with increasing time. The values given correspond roughly to oxidation in air at 30° C of $\frac{1}{4}$ -inch coal ($b = 0.8$, $C = 0.1$) and 200-mesh coal ($b = 0.37$, $C = 0.5$), respectively.

Both fine and coarse coals show very high initial rates of oxidation. The rate decreases more rapidly with fine coal so

that after seven days' oxidation the two rates become equal momentarily. At this point the fine coal has consumed oxygen to the extent of 1.03 percent by weight of pure coal, whereas the coarse coal has consumed only 0.47 percent. As the oxidation proceeds, the rate for fine coal falls to about half that of the coarse coal, with the result that, after 42 days, both will have consumed the same amount of oxygen (2 percent by weight of pure coal). Thereafter the rates of oxidation of both coals decrease continually but never reach zero.

In Fig. 3 the rate of oxidation, in grams of oxygen consumed per 100 grams of pure coal per day, is plotted against the extent of oxidation, grams of oxygen consumed per 100 grams of original pure coal. The striking decrease in the initially high rate of oxidation of fine coal is well illustrated in this figure.

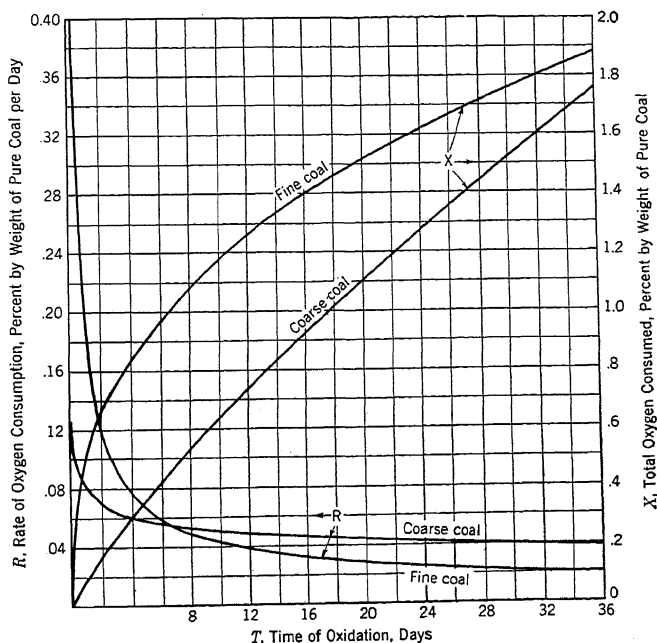


FIG. 2. Change in rate of oxidation with time of oxidation for fine coal and coarse coal at 30° C.⁴¹

The value of b (0.37) used for calculating the data for fine coal in Figs. 2 and 3 is the average of 34 different oxidation ex-

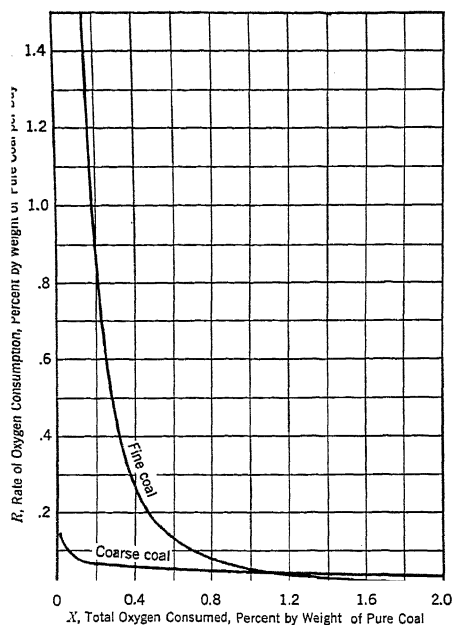


FIG. 3. Change in rate of oxidation of coal with extent of oxidation.⁴⁶

periments on 200-mesh coal reported by Graham.⁴⁶ In these experiments tests were made at temperatures ranging from 30 to 160° C on six different types of coal taken

from the Barnsley Seam, viz., Hards, Jacks, Cannel, Softs, Top Softs, and shale (82 percent ash). The results of these tests were plotted as shown in Fig. 1, and in each experiment the points fell closely along straight lines. The values of b found from the slopes of these straight lines are shown in Table I. There is no very significant variation in the value of b , either with temperature of oxidation between 30 and 140° or with the type of coal tested. The way in which the rate of oxidation of each of these particular samples of fine coal decreases with time can, with satisfactory accuracy, be expressed as follows: for any value of time (t) chosen, if the coal is oxidized twice as long the rate will be cut in half.

The values of the constant C , obtained from the data for the 30 and 100° C oxidations, are shown in Table II. These values are numerically equal to the amount of oxygen consumed by the coal sample at the end of the first day of oxidation under the indicated experimental conditions and are expressed as oxygen consumed, percent by weight of unoxidized pure coal. The ratio of each value of C to the average value of C is given in order to show for the different types of coal the percentage variation in amount of oxygen consumed. The various

TABLE II

AMOUNT OF OXYGEN CONSUMED AT THE END OF THE FIRST DAY OF OXIDATION. VALUES OF C , PERCENT BY WEIGHT OF PURE COAL (—200-MESH)

Coal	Hards	Jacks	Cannel	Barnsley Softs	Top Softs	Shale	Average *
30° C value	0.513	0.453	0.383	0.639	0.532	0.460	0.504
30° C ratio †	1.017	0.899	0.760	1.268	1.056	.914	1
100° C value	3.595	3.598	3.13	4.784	4.535	3.948
100° C ratio †	0.910	0.911	0.793	1.212	1.149	1
Average ratio	0.964	0.905	0.777	1.24	1.102	1

* Excluding shale.

† Ratio of value to average value of the five coals.

types of coal did not differ greatly in the amount of oxygen consumed in one day of oxidation. Barnsley Softs consumed 24 percent more oxygen and Cannel 22 percent less oxygen than the average.

In Table III, the rates of oxidation of these coals are compared at the end of the first day of oxidation ($t = 1$). At this time

cent by weight of pure coal per day) when each sample had consumed oxygen equivalent to 1 percent by weight of pure coal ($X = 1$). Since all samples showed about the same value of b , roughly the same ratios of rates would be found at any other value of X chosen. Upon this basis, Barnsley Softs showed a rate of oxidation 75 per-

TABLE III

RATE OF OXYGEN CONSUMPTION AT THE END OF THE FIRST DAY OF OXIDATION VALUES OF $R_{t=1}$, PERCENT BY WEIGHT OF PURE COAL (-200-MESH) PER DAY

Coal	Hards	Jacks	Cannel	Barnsley Softs	Top Softs	Shale	Average *
30° C value	0.1789	0.1776	0.1564	0.2172	0.2044	0.1709	0.1869
30° C ratio †	0.957	0.950	0.837	1.162	1.094	.915	1
100° C value	1.26	1.41	1.28	1.63	1.74	1.46
100° C ratio †	0.858	0.964	0.873	1.113	1.191	1
Average ratio	0.908	0.957	0.855	1.138	1.143	1

* Excluding shale.

† Ratio of value to average value of the five coals.

Barnsley Softs consumed oxygen at a rate 14 percent greater than the average and Cannel 15 percent less than the average. Probably the best general basis of comparison of the rates of oxidation of the various coals is found when they have all consumed the same amount of oxygen, as shown in Table IV. The values given in Table IV are the rates of oxygen consumption (per-

cent greater and Cannel 48 percent less than the average, the other types falling in this range. It should be noted that the shale sample, even though it contained 82 percent ash, showed a characteristic rate of oxidation ($R_{X=1}$) that did not differ greatly from the other types of coal (pure-coal basis), thus indicating that the ash is inert.

TABLE IV

CHARACTERISTIC RATE OF OXIDATION. OXYGEN CONSUMPTION IN PERCENTAGE BY WEIGHT OF PURE COAL (-200-MESH) PER DAY

Values of $R_X = 1$

Coal	Hards	Jacks	Cannel	Barnsley Softs	Top Softs	Shale	Average *
30° C value	0.0514	0.0520	0.0389	0.0910	0.0743	0.0459	0.06152
30° C ratio †	0.836	0.845	0.632	1.479	1.208	.747	1
100° C value	13.65	10.28	6.684	33.96	19.68	16.85
100° C ratio †	0.810	0.610	0.397	2.015	1.168	1
Average ratio	0.823	0.728	0.515	1.747	1.188	1

* Excluding shale.

† Ratio of value to average value of the five coals.

EFFECT OF TEMPERATURE

Ordinarily, temperature is by far the most important factor governing the rate of oxidation of coal. It has been found that for many chemical reactions, if $\log R$, where R is the characteristic reaction rate, is plotted against the reciprocal of the absolute temperature (T_k), the points fall along a straight line.⁴⁸ This fact is the experimental justification of the Arrhenius expression correlating reaction rate with temperature:

$$\frac{d \ln R}{dT_k} = \frac{E}{1.986T^2} \quad (5)$$

or, in its integrated form,

$$2.303 \log_{10} \frac{R_1}{R_2} = \frac{E}{1.986} \frac{1}{(T_k)_2} - \frac{1}{(T_k)_1} \quad (6)$$

where the constant E is called the energy of activation, calories per mole; R_1 is the rate of reaction at absolute temperature $(T_k)_1$ ($^{\circ}\text{C} + 273$); and R_2 is the rate of reaction at absolute temperature $(T_k)_2$.

In Fig. 4, the characteristic rates of oxidation ($R_{X=1}$) obtained from the experimental work reported by Graham are plotted against the reciprocal of the absolute temperature of the oxidation. The experimental points fall along straight lines, indicating that the Arrhenius expression (equation 5) satisfactorily shows the change in rate of oxidation with temperature.⁴⁹ However, it will be noted that bet-

⁴⁸ Glasstone, S., *Textbook of Physical Chemistry*, D. Van Nostrand Co., New York, 1940, pp. 1067-8.

⁴⁹ Two points are given at each temperature. One point is the value of $R'_{X=1}$ obtained by using the actual value of b measured in this particular oxidation experiment; the other point is $R''_{X=1}$, the value obtained by using the average value of b obtained for this coal in all the experiments. The straight line is usually drawn approximately through the average of these two points.

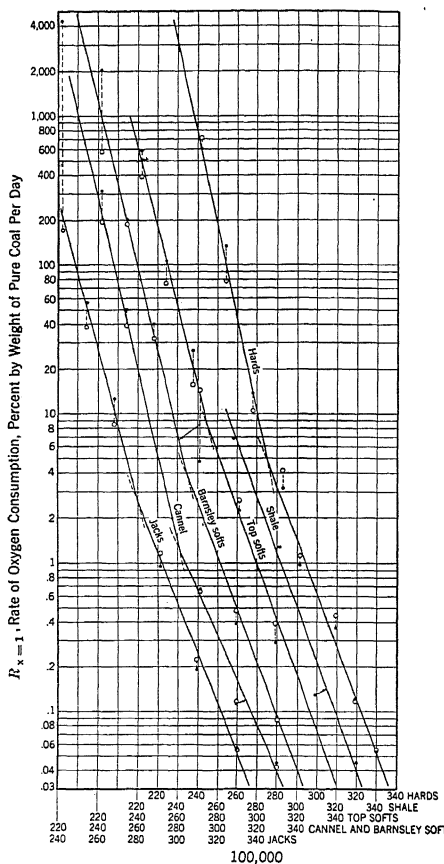


Fig. 4. Characteristic rates of oxidation as a function of temperature of oxidation.⁴⁸

ter correlation with the experimental data is obtained when two straight lines are drawn for each coal. The equations of all the straight lines shown in Fig. 4 are of the form:

$$\log R_{X=1} = m - \frac{n}{T_k} \quad (7)$$

where $R_{X=1}$ = rate of oxygen consumption in air when the sample has consumed 1 percent of its weight of oxygen, expressed as percent by weight of pure coal per day; m and n are empirical constants; and

T_k = temperature of oxidation, degrees Kelvin.

Table V gives for each coal the two sets of values of m and n , one set (m_1, n_1) for temperatures below the temperature of intersection of the two straight lines and the other set (m_2, n_2) for temperatures above the point of intersection. All these coals showed about the same rate of increase in rate of oxidation with increasing temperature. The average value of the activation

very convenient for estimating the amount of change in rate of oxidation of coal caused by any given change in the temperature of oxidation. The values shown on the vertical lines are the temperatures of oxidation, whereas those shown on the horizontal lines are the corresponding relative rates of oxidation (R). Taking an example at random to illustrate the use of the graph, at 16° C the relative rate of oxidation is 5.2 and at 29° C it is 17.0, nearly

TABLE V
VALUES OF THE CONSTANTS IN EQUATIONS 5, 6, AND 7

Coal	Hards	Jacks	Cannel	Barnsley Softs	Top Softs	Average
Point of intersection of two straight lines, °C	90.6	84.1	81.6	77.9	86.7	84.2
m_2	17.915	14.240	15.999	16.327	15.605	16.0172
n_2	6,259	4,934	5,660	5,519	5,338	5,542
m_1	10.635	9.997	8.732	10.936	11.247	10.3094
n_1	3,613	3,418	3,073	3,629	3,750	3,497
E_2	28,633	22,571	25,892	25,248	24,420	25,353
E_1	16,528	15,636	14,058	16,601	17,155	15,998

energy for temperatures below 84° C is 16,000 calories per mole and for higher temperatures 25,350 calories per mole. Chukhanov⁵⁰ reported values of 20,000 to 25,000 calories for the oxidation of charcoal at temperatures around 750° C and below. Meyer⁵¹ reported values of 20,000 to 30,000 for temperatures up to 1,520° K. Kreulen and others⁵² reported an average value of 27,600 for coals in the temperature range of 220 to 260° C.

Using the average values of constant n given in Table V, the data shown in Fig. 5 were calculated. This figure will prove

a threefold increase in rate of oxidation for a temperature rise of only 13° C (23° F).

The data in Fig. 5 show that, if two identical samples of coal have consumed the same amount of oxygen and one is oxidized at 160° C in an ample supply of air, it will momentarily consume oxygen 544,000 times as fast as the sample in air at 0° C. The rate of oxidation will, of course, decrease much more rapidly with time at the higher temperatures. For example, using the average values of b and C (Tables I and II), only 36 minutes' exposure to air at 100° C is required for the coal to consume 1 percent of its weight of oxygen ($X = 1$), whereas at 30° C 6.3 days are required. Furthermore, at 100° C, the rate of oxidation falls off to half the value it had at $X = 1$ in 1.2 hours' more oxidation, whereas it requires 12.6 additional days'

⁵⁰ Chukhanov, Z., *Tech. Phys. U.S.S.R.*, **5**, No. 7, 41-58, 511-24 (1938); *Fuel*, **18**, 292-302 (1939), **19**, 17-20, 49-50, 64-7 (1940).

⁵¹ Meyer, L., *Z. physik. Chem.*, **B17**, 385-404 (1932). Tu, C. M., Davis, H., and Hottel, H. C., *Ind. Eng. Chem.*, **26**, 749-57 (1934).

⁵² Kreulen, D. J. W., Krijgsman, C., and Horst, D., *Fuel*, **17**, 243-58 (1938).

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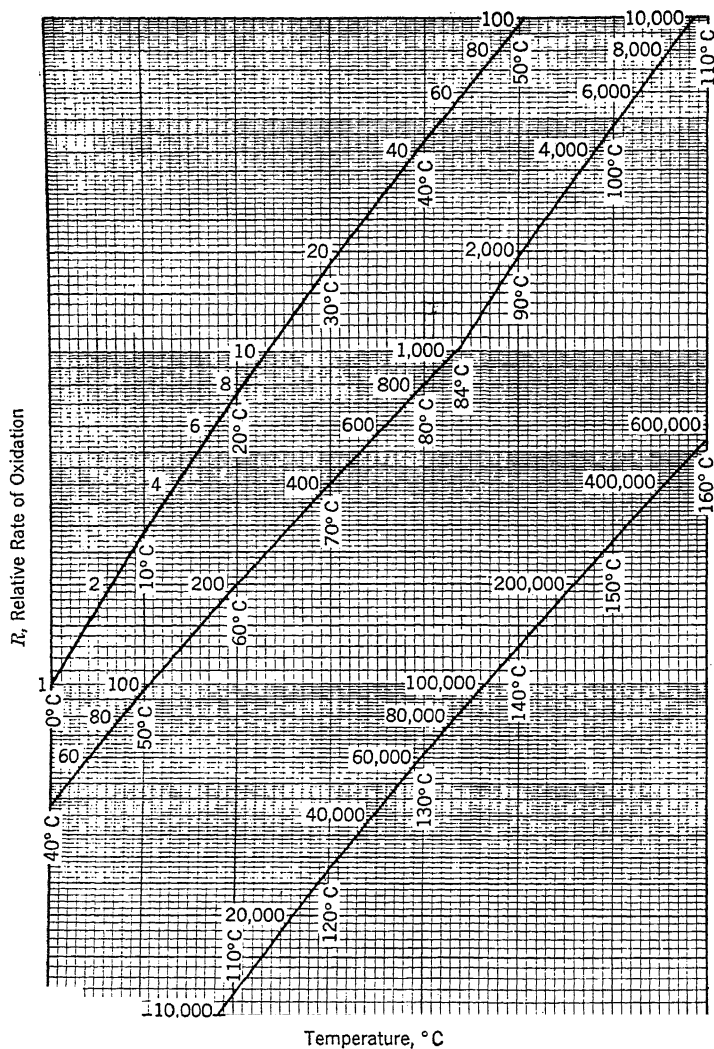


FIG. 5. Relative rates of oxidation as a function of temperature of oxidation.

oxidation at 30° C to halve the rate. The decrease in rate with increasing extent of oxidation is a very potent factor, tending to compensate for the enormous increase in rate with increasing temperature. This is especially true of fine coal, where the rate varies inversely with the 1.7 power of the extent of oxidation (X).

According to the data shown in Fig. 5, the rate of oxidation increases by a factor of 2.2 for each 10° C rise in temperature between 30 and 100° C. Schmidt and Elder,⁴⁵ working with 0 to $\frac{1}{4}$ -inch Pittsburgh coal, found a value of about 1.7 ($E = 11,000$) for this temperature range. The data given in Fig. 5, based upon the

work of Winnill and Graham,⁴⁶ have the decided advantage of representing the results of a large number of tests so that they are probably the best values. However, it remains to be proved whether or not coal of larger particle size than 200-mesh would show a different temperature coefficient. In the discussion of effective surface area which follows later, it will be shown that it is possible that the temperature coefficients will prove to be smaller for larger particles.

Other temperature coefficients have been reported in the literature, but since they are not based on coal at equal states of oxidation they are not directly comparable with themselves or with the values given in Fig. 5. For example, Parr⁵³ presented a graph based upon the "absorption capacity" of finely divided coal at varying temperatures—"diagrammatic in character, it is, in fact, the assembly of data from many experiments and accurately expresses the relative behavior of bituminous coals at the various temperature ranges indicated." In this graph, "cubic centimeters of oxygen absorbed per gram of coal" are plotted against temperature, degrees Centigrade, from 0 to 175° C. Assuming that the reported amounts of oxygen were consumed in a certain time so that the values given are actually rates of oxidation averaged over a definite time which was the same for all samples, then the average energy of activation over the range 50 to 150° C proves to be about 6,000 calories, which corresponds to a temperature factor of about 1.3 for a 10° C rise in temperature.

However, when all samples are oxidized for the same time the samples oxidized at the higher temperatures have correspondingly much higher final (and average) values of X , so that such a temperature

factor, if used at all, must be used very carefully. If the results of Graham are calculated upon this basis, a factor of about 1.34 for 10° C rise in temperature is obtained. Tideswell and Wheeler⁵⁴ reported a value of 1.36 upon this basis. The results of Porter and Ralston⁵⁵ indicate an average value of 1.46 for the range from 80 to 160° C. In general, the agreement between different workers is better than might be expected, considering the faulty basis of comparison.

EFFECT OF PARTICLE SIZE ON THE RATE OF OXIDATION

The interaction of oxygen with coal takes place on the surface of the coal. Consequently, the greater the extent of surface area per unit weight of coal exposed to air, the higher is the rate of oxidation per unit weight of coal. The surface area per unit weight of coal, or the specific surface of the coal, increases rapidly with increasing subdivision of the coal. Figure 6 will be found very convenient for making quick estimates of the specific surface of various Tyler screen fractions of coal. The data for making this graph were obtained by Needham and Hill⁵⁶ in an excellent research on this subject. The following example illustrates the use of the graph to obtain the specific surface area of any screen fraction: fraction 80 to 100 mesh, average 90 mesh, specific surface corresponding to 90 mesh on graph, 50 square meters per kilogram. This compares well with the value of 48.7 square meters per kilogram reported by Needham and Hill for this screen fraction. The specific sur-

⁵⁴ Tideswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **127**, 125-32 (1925).

⁵⁵ Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper* **65** (1914), 28 pp.

⁵³ Parr, S. W., *Ind. Eng. Chem.*, **17**, 120-3 (1925).

⁵⁶ Needham, L. W., and Hill, N. W., *Fuel*, **14**, 226 (1935).

face of any coal sample can be estimated from its screen analysis by this method.

The data in Fig. 6 indicate that if 1-inch coal is crushed to 250-mesh size the specific surface area increases from about 0.24 to 230 square meters per kilogram, or roughly a thousandfold. Little accurate informa-

fine coal. However, the results give probably the best information available at present on the effect of particle size. In Table VI are given the values of the oxidation rate constants, the characteristic rate of oxidation ($R_{X=1}$), and the estimated specific surface area of the samples. In Fig. 7,

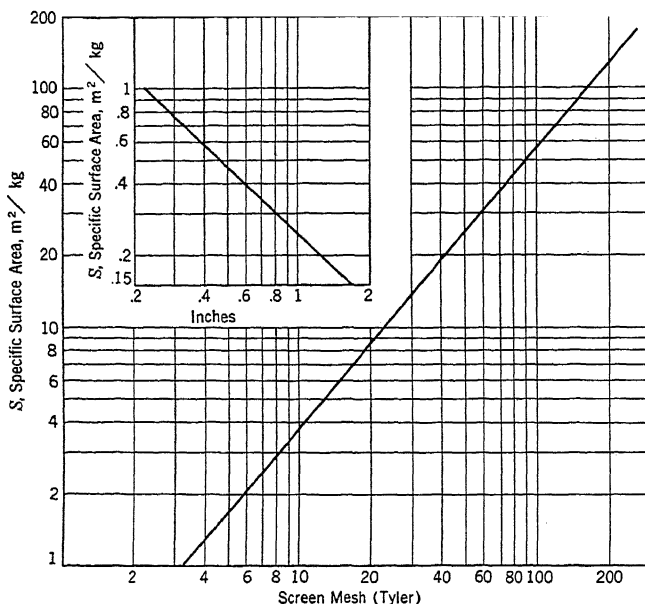


FIG. 6. Specific surface area of coal particles as a function of size.

tion has been published on the rates of oxidation of various sizes of coal, but from the information available it is apparent that increasing the surface a thousandfold does not result in a thousandfold increase in rate of oxidation, as is often implicitly assumed by various writers on the subject. Winmill⁴⁶ measured the rates of oxidation at 30 and 50° C of coal in four different particle-size classifications, namely, 2 to 10 mesh, 10 to 30 mesh, 30 to 60 mesh, and through 200 mesh. The extremely low rate of oxidation of the coarse coal made accurate measurements difficult and required modification of the procedure followed for

the characteristic rate of oxidation ($R_{X=1}$) is plotted against the specific surface (S) on log-log scale. The points fall along straight lines about as closely as might be expected, considering the high probable error in the estimations of both rate and specific surface. Three straight lines are drawn for the different coals and different temperatures of oxidation. The results may be expressed as follows:

$$R_{X=1} = kS^{0.327} \cong k\sqrt[3]{S}, \quad (8)$$

where $R_{X=1}$ = rate of oxygen consumption in air when the sample had consumed 1 percent of its weight of oxygen, grams of

TABLE VI

EFFECT OF PARTICLE SIZE ON RATE OF OXIDATION

Mesh	2-10 *		10-30	30-60	Minus 200		
Specific surface, <i>S</i> , square me- ters per kilogram	0.55		7.8	24	314		
Coal	Barnsley Hards		Barnsley Softs	Barnsley Hards	Barnsley Hards	Barnsley Hards	Barnsley Softs
Temperature, °C	30	50	30	30	30	30	50
<i>b</i>	0.556	0.56 †	0.68	0.357	0.385	0.349	0.349
<i>C</i>	.08908	.293	.0653	.368	.391	.513	.927
	.00718	.0369	.0121	.0217	.0336	.0514	.2806

* Sample prepared by sizing coal to just pass a 2-mesh screen, but fines so produced and retained on a 10-mesh screen were mixed with the larger pieces.

† Assumed value.

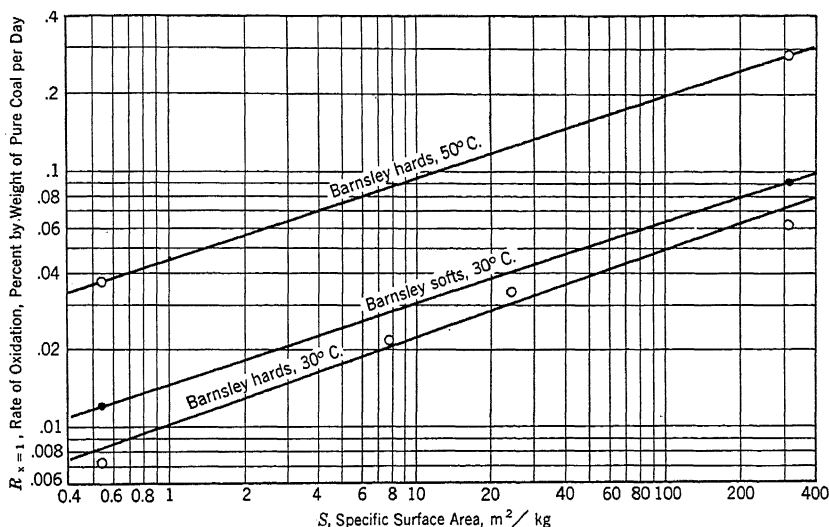


FIG. 7. Characteristic rates of oxidation of Barnsley Seam coals having different specific surface areas.⁴⁶

oxygen per 100 grams of original pure coal per day; k = a constant; and S = specific surface area, square meters per kilogram. The value of k depends on the coal tested and also the temperature of oxidation (Fig. 5). At 30° C, the average value of k for the coals tested was 0.0094.

The results indicate that the rate of oxidation of coal in air at low temperatures is proportional to the cube root of the specific surface area of the sample. The reader must remember that this relationship is tentative, resting upon a very limited amount of experimental data. How-

ever, it should prove of value until new and better information is available.⁵⁷ According to this relationship, the previously mentioned thousandfold increase in surface area obtained when 1-inch coal is crushed to 250-mesh size would be expected to cause only a tenfold increase in the rate of oxidation at these temperatures. These results make it clear that owing to porosity a total area that is the sum of the internal and external area must take part in the oxidation reaction at low temperatures. There is great need for further experimentation to test this tentative conclusion. At combustion temperatures it is entirely possible that the value of the exponent in equation 8 approaches unity, as is often assumed.⁵⁰

EFFECT OF OXYGEN CONCENTRATION IN GAS PHASE ON RATE OF OXIDATION

Work at the Bureau of Mines⁴⁵ on several coals (0- to 1/4-inch) oxidized at 99.3°C showed that, when the percentage of oxygen in air is decreased from its normal value, the decrease in the rate of oxidation is proportional to the percentage of oxygen in the air raised to the 0.61 power, or

$$R_{X=\text{constant}} = d[\text{O}_2]^{0.61} \quad (9)$$

where $R_{X=\text{constant}}$ = rate of oxidation at any given value of X ; d = a constant; and $[\text{O}_2]$ = percentage by volume of oxygen in the air.

Winmill found a value of 0.5 for the exponent in equation 9 for coal oxidized at 30°C.⁴⁶ On the other hand, analysis of the data obtained by Porter and Ralston⁵⁵ on the oxidation at 200°C in air with reduced oxygen content shows that the rate varies with the 0.71 power of the oxygen concentration.⁴⁵

CHARACTERISTIC RATES OF OXIDATION OF VARIOUS COALS

With the aid of the relationships developed in the discussion of the effect of the various conditions of oxidation upon the rate of oxidation, it is possible to convert the rates of oxidation observed by various workers to a common basis of comparison, that is, to standard conditions. Upon this common basis the rate of oxidation of a coal would be a characteristic of the coal only and so called the characteristic rate of oxidation; furthermore, these rates could still be reported in fundamental units. However, before standard conditions can be specified more closely, further research is needed to allow greater accuracy in the prediction of rates of oxidation under conditions considerably different from those under which the data were obtained.

In Fig. 8 (lower graph) the characteristic rates of oxidation in air at 99.3°C of nine coking coals⁵⁸ (0- to 1/4-inch) are plotted on semilog scale against the percentage of oxygen (O_2) plus the percentage of pyritic sulfur (S_p) in the fresh coal (pure-coal basis). The points fall along a straight line, the slope of which shows higher rates of oxidation for coals of higher oxygen plus pyritic sulfur content. These tests were made upon samples of coal that were representative of the coal seams. The sources and analyses of these coals are given in Table VII. It may be noted that, as the content of pyritic sulfur was low compared with the content of oxygen, a graph very similar to those in Fig. 8 is obtained if merely the percentage of oxygen in fresh coal is plotted. Furthermore, since the percentage of oxygen in fresh coal, in general, increases with increasing content of volatile matter, a curve very similar in

⁵⁷ See p. 107 of ref. 32.

⁵⁸ Schmidt, L. D., *Iron Steel Engr.*, 18, No. 3, 64-70 (1941).

type is obtained when the rate of oxidation is plotted against the percentage of volatile matter in fresh coal.⁵⁹

In the upper graph of Fig. 8 the characteristic rate of oxidation of the same coals is shown plotted on semilog scale against an empirical grouping of the coal constituents. In this group $(C)_o$ is the percentage

the coal and characteristic rate of oxidation would not be as good. However, the general tendency for increased characteristic rates of oxidation with increased oxygen and volatile-matter contents is observed throughout the range from anthracite to lignite,⁶⁰ even though there are exceptional coals.⁴⁶

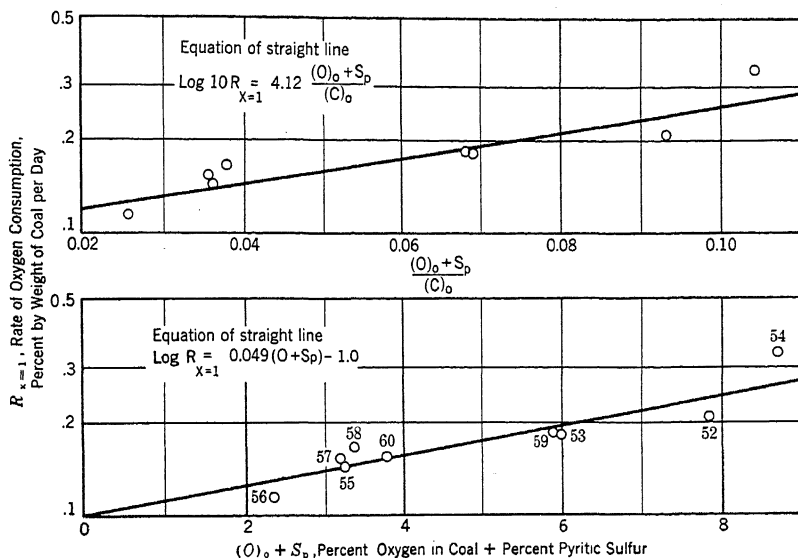


FIG. 8. Characteristic rates of oxidation of American coals as functions of analysis.⁵⁸

of carbon in fresh coal upon the pure coal basis.

The coals represented in Table VII and Fig. 8 cover nearly the whole range of analysis⁴⁵ of ordinary commercial coking coals, yet there is only a threefold range in characteristic rate of oxidation. If the field were enlarged to include noncoking coals there would, of course, be a much larger range in the rate of oxidation, and probably the correlation between analysis of

CONTENT OF PYRITES AND CHARACTERISTIC RATES OF OXIDATION

Iron disulfide occurs in coal in two crystalline forms, pyrite and marcasite, both of which oxidize; for the present purpose both will be called pyrites. In all probability pyrites occur in all coal,⁶¹ particles

⁵⁹ Godbert, A. L., and Belcher, R., *17th Ann. Rept., Safety in Mines Research Board (London)*, 1938, 44 pp. Bunte, K., Brückner, H., and Bender, W., *Gas- u. Wasserfach*, **81**, 178-83, 200-3 (1938).

⁶⁰ Graham, J. I., *Colliery Guardian*, **140**, 902-4, 1008-9 (1930). Olin, H. L., and Waterman, W. W., *Ind. Eng. Chem.*, **28**, 1024-5 (1936). Olin, H. L., Conrad, P. L., Krouse, M., and Whitson, R. E., *Ind. Eng. Chem., Anal. Ed.*, **11**, 489-91 (1939).

⁶¹ Lomax, J., *Trans. Inst. Mining Engrs.*, **46**, 592-635 (1913-4); *Colliery Guardian*, **129**, 1317-8 (1925). Thiessen, R., *Trans. Am. Inst. Mining Met. Engrs.*, **63**, 913-26 (1919-20).

CHANGES IN COAL DURING STORAGE

TABLE VII

SOURCE AND ANALYSIS OF NINE COKING COALS

	Coal Number								
	54 *	52 †	53 ‡	59 §	60	58 ¶	55 **	56 ††	57 ††
Petrographic analysis, percent									
Type									
Bright	33	84	73	86	93	36	81	88	90
Semisplint	14	13	16	14	5	53	15	2	5
Splint	53	3	11	0	2	0	4	10	0
Cannel	11	5
Components									
Anthraxylon	31	63	43	67	68	30	60	60	57
Translucent attritus	41	22	38	26	24	49	23	20	30
Opaque attritus	26	12	15	6	7	19	12	11	11
Fusain	2	3	4	1	1	2	5	9	2
Chemical analysis, dry basis, percent									
Volatile matter	38.2	37.3	33.1	30.1	25.4	22.0	22.1	17.7	17.8
Fixed carbon	57.7	56.4	62.3	61.4	68.1	69.5	74.9	75.6	75.3
Ash	4.1	6.3	4.6	8.5	6.5	8.5	3.0	6.7	7.4
Hydrogen	5.3	5.2	5.2	5.0	5.0	4.6	4.8	4.2	4.4
Carbon	80.1	79.2	82.4	79.1	82.8	81.5	87.2	85.0	83.7
Nitrogen	1.4	1.6	1.5	1.4	1.4	1.2	1.5	1.2	1.4
Oxygen	8.5	6.2	5.6	5.3	3.5	2.6	2.8	2.3	2.0
Sulfur									
Pyritic	0.01	0.85	0.09	0.18	0.02	0.68	0.25	0.06	0.6
Nonpyritic	0.59	0.65	0.61	0.57	0.74	0.92	0.45	0.54	0.5
Friability, percent	14.4	27.1	31.0	55.1	74.6	56.6	62.2	68.4	...
Heating value, calories per gram	7,894	7,892	8,133	7,822	8,111	7,950	8,444	8,128	8,011

* High Splint Seam, Closplint mine, Closplint, Harlan County, Ky.; rank, high-volatile A.

† Pittsburgh Seam, Bruceton mine, Bruceton, Allegheny County, Penna.; rank, high-volatile A.

‡ Pond Creek Seam, Majestic mine, Majestic, Pike County, Ky.; rank, high-volatile A.

§ Upper Freeport Seam, Morgantown District, Monongalia County, W. Va.; rank, high-volatile A.

|| Lower Freeport Seam, Indiana County, Pa.; rank, medium-volatile.

¶ Lower Banner Seam, Keen Mountain mine, Hangar, Buchanan County, Va.; rank, medium-volatile.

** Sewell Seam, Wyoming mine, Wyoming, Wyoming County, W. Va.; rank, medium-volatile.

†† Pocahontas No. 3 Seam, Buckeye No. 3 mine, Stephanson, Wyoming County, W. Va.; rank, low-volatile.

‡‡ Pocahontas No. 4 Seam, No. 4 mine, Affinity, Raleigh County, W. Va.; rank, low-volatile.

ranging from a few microns in diameter to pyritic boulders several feet in diameter.⁶²

There has been considerable controversy

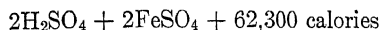
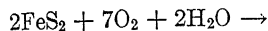
⁶² Yancey, H. F., and Fraser, T., *Ind. Eng. Chem.*, **13**, 35-7 (1921); *Univ. Illinois Eng. Exp. Sta., Bull.* **125** (1921), 92 pp. Yancey, H. F., and Parr, S. W., *Ind. Eng. Chem.*, **16**, 501-8 (1924).

on the subject of the effect of pyrites on the observed rate of oxidation of coal at low temperatures, especially as to whether or not the presence of pyrites causes spontaneous ignition.^{21, 63} There is no disagree-

⁶³ Bone, W. A., and Himus, G. W., *Coal, Its Constitution and Uses*, Longmans, Green & Co., London, 1936, pp. 194-205.

ment over the fact that pyrites under ordinary storage conditions consumes oxygen and evolves heat in the process. Differences of opinion arise in evaluating the magnitude and importance of the effects.⁶⁴

Pyrites oxidize as follows:



It will be noted that water enters into the reaction as written and that a considerable quantity of heat is evolved.

Winmill⁶⁵ measured the rate of oxidation of pyrites in moist air and found rates higher than those of coal of the same particle size. In one week of oxidation, the rate decreased to about 25 percent of the initial rate, whereas for coal in the same time the rate decreased to 7 percent of the first value observed. Upon washing the pyrites with water, the rate increased to a point near the original rate. He found that the rate was proportional to the surface exposed and to the percentage oxygen in the air, and that this rate doubled for every 10° C rise in temperature from 30 to 60° C. In later experiments,⁴⁶ coals of a considerable range in pyrites content were oxidized in moist air and the amount of oxygen consumed by pyrites was determined by measuring the increase in amount of sulfate caused by oxidation. Winmill concluded that as long as the pyrites were all in the form of "brass" or as bright thin veins, they played a small part in the total consumption of oxygen by the coal sample. If, however, the pyrites were present in high proportion and in a finely divided state, they played a very important role.

⁶⁴ Graham, J. I., *Trans. Inst. Mining Engrs.*, **67**, 100-13 (1924). Li, S. H., and Parr, S. W., *Ind. Eng. Chem.*, **18**, 1299-1304 (1926).

⁶⁵ Winmill, T. F., *Trans. Inst. Mining Engrs.*, **51**, 500-9 (1915-16).

Burke and Downs,⁶⁶ working with cubes of pyrites rotating in normal hydrochloric acid solution with oxygen circulating through the system, found that the reaction rate doubled for a 25° C rise in temperature. They showed that the reaction rate was inhibited by sulfate ions, which were adsorbed on the reacting surfaces. Consequently, the rate of reaction in dry oxygen was considerably less than in aqueous solutions that removed the inhibitor. The storage of coal in a place where it would be wet repeatedly by rains presumably would increase the rate of oxidation of pyrites. Because of this effect, care must be taken in interpreting laboratory results where the samples were not subjected to occasional wetting. Pyrites exposed in a saturated atmosphere have been reported to oxidize more rapidly than when immersed in water.⁶⁷ It is interesting to note that small amounts of chlorine greatly accelerate the rate of oxidation of pyrites under water.⁶⁸

MacPherson, Simpkin, and Wild⁶⁹ observed the oxidation in the laboratory of coals rich in pyrites and concluded that, although pyrites may assist in a minor degree in the self-heating of coal, their most important effect is the disintegration caused in the coal by its oxidation to bulkier products.⁷⁰

The consensus of opinion among modern writers⁶³ seems to be that, since the percentage of weight of pyrites present in commercial coals is so small, the influence

⁶⁶ Burke, S. P., and Downs, R., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 425-42 (1938).

⁶⁷ Nicolls, J. H. H., and Swartzman, E., *Can. Dept. Mines, Mines Branch Rept. 737* (1934), pp. 58-62.

⁶⁸ Nelson, H. W., Snow, R. D., and Keyes, D. B., *Ind. Eng. Chem.*, **25**, 1355-8 (1933).

⁶⁹ MacPherson, H., Simpkin, S. N., and Wild, S. V., *Safety in Mines Research Board (London), Paper 47* (1928), 24 pp.

⁷⁰ See p. 16 of ref. 2 and pp. 31-2, 46 of ref. 12.

of pyrites is a subordinate factor⁷¹ in the changes taking place in storage of coal. However, the opinion persists, especially among men who actually store coal, that pyrites serve as the pilot light to start the process of spontaneous ignition.¹⁷

NATURAL OR BED MOISTURE CONTENT⁷² AND CHARACTERISTIC RATE OF OXIDATION

In general, the higher the natural or bed moisture content of coals, the higher is the characteristic rate of oxidation.^{46, 60} Of course, in general, high bed moisture content is usually associated with high oxygen content, both decreasing with increasing rank of coal so that either constituent may be the important factor as far as present knowledge goes.⁷³

A clear distinction should be made between this general increase in characteristic rate of oxidation with increasing natural moisture content of coals and the much different situation of the effect on rate of oxidation of varying amounts of water added to a given coal. In this connection Katz and Porter⁷⁴ compared the rates of oxidation of dry and moist coal at 25° C. The dry tests were made with coal dried in vacuo or in nitrogen over phosphorus pentoxide, which also was present in the oxidation flask. The results indicated that the effect of moisture was very slight. However, Graham⁴⁶ reported that removal of the last traces of water does effect a considerable reduction in the rate of oxidation. The question of the effect of last traces of water is still in dispute.⁷⁵ This dispute is

⁷¹ Stopes, M. C., and Wheeler, R. V., *Fuel*, **2**, 29-41, 83-92, 122-32 (1923).

⁷² Stansfield, E., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, **101**, 125-47 (1932).

⁷³ Lea, F. M., *Fuel*, **7**, 430-44 (1928).

⁷⁴ Katz, S. H., and Porter, H. C., *U. S. Bur. Mines, Tech. Paper* **172** (1917), 25 pp.

⁷⁵ Mahler, P., *Compt. rend.*, **150**, 1521-3 (1910). Galloway, W., *Colliery Guardian*, **128**, 1000 (1924).

rather academic, since water is one product of the oxidation reaction and it would probably be impossible to maintain the coal entirely free of traces of water. There is general agreement that if some water is present small variations in water content have little effect on the rate of oxidation. As mentioned previously, a large excess of water revives the oxidation process of partly spent pyrites by washing off the inhibiting sulfate ions.

PETROGRAPHIC ANALYSIS AND CHARACTERISTIC RATE OF OXIDATION

The characteristic rates of oxidation of the nine coking coals shown in Fig. 8 exhibit no well-defined correlation with the petrographic analyses of these coals given in Table VII. This is an indication that the various petrographic constituents oxidize at rates of the same order of magnitude. Graham measured the rates of oxidation of the various types of coal found in the Barnsley Seam. It will be noted in Table IV that the greatest difference in rate was between cannel coal and Softs, the Softs oxidizing 3.4 times as fast as the cannel.

Lefebvre and Faivre,⁷⁶ using an apparatus that permitted very precise results, found that vitrain and durain oxidized at about the same rate at 250° C, but that fusain oxidized at one-tenth this rate.

Tideswell and Wheeler and Stopes⁷⁷ measured the rates of oxidation for the four visible ingredients of banded coal and found the following order of decreasing oxidizability: fusain, vitrain, clarain, and durain. At 100° C, there was no great difference in rate of oxidation of the various constituents, but at 15° C fusain (previ-

⁷⁶ Lefebvre, H., and Faivre, R., *Compt. rend.*, **203**, 881-3 (1936).

⁷⁷ Tideswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **117**, 794-801 (1920). Stopes, M. C., and Wheeler, R. V., *Fuel*, **2**, 122-7 (1923).

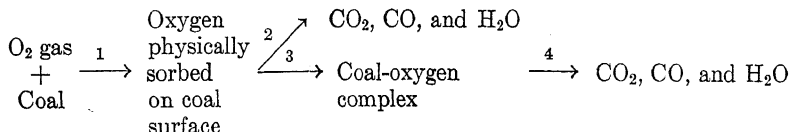
ously evacuated) showed a rate of oxygen consumption greater than the other constituents. Pohl and Ferrari⁷⁸ deduced that vitrain is the most dangerous constituent in connection with spontaneous ignition. Francis⁷⁹ reported the order of decreasing oxidizability to be vitrain, clarain, and durain, and that fusain is very oxidizable.

Francis and Wheeler⁸⁰ found that both the extracts and residue of coal oxidize in oxygen at 100° C.

It can be concluded that all the constituents of coal (except water and ash) oxidize when exposed to air at low temperatures.⁷⁹ Although vitrain or anthraxylon is apparently the most reactive constituent, nevertheless, all constituents, including fusain,⁸¹ play a very important part in the reaction.

MECHANISM OF THE OXIDATION REACTION AND THE PHYSICAL STRUCTURE OF COAL

The mechanism of the reaction between gaseous oxygen and coal at low temperatures is not simple. It probably may be expressed somewhat as follows:



At present little is known about the individual steps in this process. It is commonly accepted^{54, 82} that, at low temperatures (presumably below, say, 200° C) and under ordinary conditions, step 1 is extremely rapid compared to the succeeding

steps. Consequently, the rates of reaction of the succeeding steps, 2, 3, and 4, are those that control the overall rate of consumption of oxygen.

Experimental work has shown that coal gains in weight upon oxidation,⁸³ sometimes as much as 12 percent of its original weight.⁸⁴ This shows that the weight of oxygen remaining in the coal-oxygen complex is greater than the weight of carbon and hydrogen evolved in gaseous products.

In experiments where fine coals are oxidized at constant temperatures below their "ignition point" (below 200° C), in most instances roughly one-half the oxygen consumed remains upon the coal, the other half appearing in the gaseous products as carbon dioxide, carbon monoxide, and water.⁸⁵ Therefore, it can be reasoned that steps 2 and 4, taken together, apparently proceed at about the same rate as step 3. Since in this case step 4 by itself is slower than step 3, the net result is that the amount of the solid called the "coal-oxygen

complex" increases steadily with increasing oxidation of the coal.

The properties of the "coal-oxygen complex" are not well known. One gathers from reading the literature⁸⁵ on the sub-

⁷⁸ Pohl, H., *Kohle u. Erz*, **33**, 421-4 (1936).
⁷⁹ Ferrari, B., *Glückauf*, **74**, 765-74 (1938).

⁷⁹ Francis, W., *Proc. Am. Gas Assoc.*, **1927**, 1392-8.

⁸⁰ Francis, W., and Wheeler, R. V., *Fuel*, **11**, 356-9 (1932).

⁸¹ Künle, O., *Brennstoff-Chem.*, **9**, 295-8 (1928).

⁸² Yohe, G. R., and Harman, C. A., *J. Am. Chem. Soc.*, **63**, 555-6 (1941).

⁸³ Parr, S. W., and Milner, R. T., *Ind. Eng. Chem.*, **17**, 115-7 (1925); *Fuel*, **5**, 298-301 (1926). Kreulen, D. J. W., *Fuel*, **5**, 345-6 (1926). Parr, S. W., *The Analysis of Fuel, Gas, Water and Lubricants*, McGraw-Hill Book Co., New York, 1932, 371 pp.

⁸⁴ Donnelly, J. T., Foott, C. H., Nielsen, H., and Reilly, J., *J. Soc. Chem. Ind.*, **47**, 1-4T, 139-43T, 189-92T (1928), **48**, 38-40T, 101-5T (1929).

⁸⁵ Wheeler, R. V., *J. Chem. Soc.*, **113**, 945-55 (1918). Tideswell, F. V., and Wheeler, R. V.,

ject that the complex is very unstable.⁵⁵ However, it is apparently fairly stable, at least at or below the temperature of its formation, as samples of oxidized coal can be stored for a long time in tightly stoppered bottles without appreciable change in analysis. This solid complex apparently is not of definite stoichiometric composition. In contact with air during the oxidation experiments, it probably consumes oxygen in much the same way as coal, thus leading to step 4.

The initial rapid decrease in total rate of oxygen consumption with time after exposure of a fresh surface to air (Figs. 2 and 3) suggests that the coal-oxygen complex may be fairly resistant to oxidation and so has the effect of merely covering the active surface of coal, thus decreasing the availability of oxygen to the fresh coal underneath. The coal-oxygen complex is possibly similar to those formed when carbon⁸⁶ or wood charcoal⁸⁷ is exposed to oxygen and no doubt has something in common with the peroxides found in the oxidation of hydrocarbons and other organic materials.⁸⁸

Exhaustive low-temperature oxidation of fine, bright coal results in a product that is almost completely soluble in caustic solutions.⁸⁹ In fact, the amount of caustic soluble material formed by the low-temperature oxidation of coal is a good measure of the extent of oxidation of the coal.¹³ These caustic soluble materials are called variously ulmins, ulmic acid, humins, and humic acids,⁹⁰ and one would presume from their method of preparation that they are closely related to the original coal-oxygen complex. After precipitation from solution with acid, these solids consume oxygen from air at low temperatures and are of indefinite composition.

When oxidized coal is heated to temperatures somewhat below the normal decomposition temperature of coal, or as oxygen is added continuously in the oxidation reaction, the coal-oxygen complex decomposes, forming carbon dioxide, carbon monoxide, and water,⁹¹ the components ap-

goyne, J. H., *Proc. Roy. Soc. (London)*, **A175**, 539-63 (1940).

⁸⁹ Kreulen, D. J. W., *Brennstoff-Chem.*, **8**, 340-3 (1927). Yohe, G. R., and Harman, C. A., *Trans. Illinois State Acad. Sci.*, **32**, No. 2, 134-6 (1939).

⁹⁰ Eccles, A., Kay, H., and McCulloch, A., *J. Soc. Chem. Ind.*, **51**, 49-59T (1932). Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **57**, 312-6 (1935). Weiler, J. F., *Fuel*, **14**, 190-6 (1935); *J. Am. Chem. Soc.*, **58**, 1112-4 (1936). Gillet, A. C., *Rev. universelle mines*, **14**, 782-6 (1938). Morgan, G. T., and Jones, J. I., *J. Soc. Chem. Ind.*, **57**, 289-92 (1938).

⁹¹ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **1927**, 2958-67. Coles, G., and Graham, J. I., *Fuel*, **7**, 21-7 (1928); **12**, 304-12 (1933). Terres, E., and Voituret, K., *Gas- u. Wasserfach*, **74**, 97-101, 122-8, 148-54, 178-82 (1931). Hal-dane, J. S., and Makgill, R. H., *J. Soc. Chem. Ind.*, **53**, 359-67T (1934); *Gas World*, **102**, 14 (1935). Lefebvre, H., and Faivre, R., *Compt. rend.*, **203**, 881-3 (1936). Chukhanov, Z., *Tech. Phys. (U.S.S.R.)*, **5**, No. 7, 511-24 (1938); *Fuel*, **18**, 292-302 (1939), **19**, 17-20, 49-50 (1940). Newall, H. E., *ibid.*, **17**, 292-9 (1938). Sanders, H., *Glückauf*, **74**, 921-6 (1938). Scott, G. S., and Jones, G. W., *U. S. Bur. Mines, Rept. Inves-*

ibid., **115**, 895-902 (1919). Haslam, R. T., *Fuel*, **7**, 253-7 (1928). Berl, E., and Winnacker, K., *Z. physik. Chem.*, **A148**, 261-83 (1930). Bunte, K., and Brückner, H., *Angew. Chem.*, **47**, 84-6 (1934). Hock, H., and Schrader, O., *Brennstoff-Chem.*, **17**, 312 (1936). Krym, V. S., *Khim. Tverdogo Topliva*, **8**, 461-72 (1937); *Chem. Abs.*, **32**, 1428 (1938). Krym, V. S., and Semnikhin, S. I., *Khim. Tverdogo Topliva*, **8**, 782-5 (1937); *Chem. Abs.*, **32**, 2319 (1938). Scott, G. S., Jones, G. W., and Cooper, H. M., *U. S. Bur. Mines, Rept. Investigations*, **3398** (1938), 8 pp. Yohe, G. R., and Harman, C. A., *J. Am. Chem. Soc.*, **63**, 555-6 (1941).

⁸⁶ Langmuir, I., *J. Am. Chem. Soc.*, **37**, 1154-6 (1915). Strickland-Constable, R. F., *Fuel*, **19**, 89-93 (1940).

⁸⁷ Rhead, T. F. E., and Wheeler, R. V., *J. Chem. Soc.*, **103**, 461-89 (1913).

⁸⁸ Postovskii, I. Y., and Postovskaya, A., *Coke and Chem. (U.S.S.R.)*, **4**, No. 12, 7-10 (1934); *Chimie et industrie*, **35**, 555 (1936). Plissov, A. K., *Bull. soc. chim.*, **3**, 1274-81 (1936). Bur-

pearing in various ratios.⁶³ Sometimes more complex decomposition products are found.⁹²

It has been reported that, upon evacuation at 200° C, some decomposition and evolution of carbon dioxide, carbon monoxide, and water take place and the characteristic rate of oxidation of the coal is restored to values near the original values for fresh coal.⁹³ However, the work of Donnelly and others⁸⁴ showed that a coal-oxygen complex is formed and is stable at 200° C. The properties of the complex may differ greatly with the conditions of formation and with difference in coal type. Studies of the initial appearance of carbon dioxide⁹⁴ when fine coal is heated rapidly in oxygen showed that, for extensively pre-oxidized Illinois coal, carbon dioxide appeared first at about 125° C, whereas with fresh coal it appeared first at about 93° C. As both the fresh and the oxidized coals were heated in oxygen, these results are not a good criterion as to the stability of the coal-oxygen complex, except to indicate that the complex is not extremely unstable at these temperatures. In this connection, it should be noted that Coles and Graham⁹⁵ have shown that preheating coals to 300° C in vacuo doubled the characteristic

rate of oxidation of some coals, although other coals were not greatly affected.

Interaction of oxygen with coal takes place on the solid-gas interface. Because of the colloidal nature of coal,⁹⁶ the superficial external surface area of a solid sphere or cube of coal of known dimensions, however, by no means equals the area of the solid-gas interface that takes part in the reaction with oxygen at low temperatures. In other words, coal is to a certain extent porous, so that low-temperature oxidation occurs on a surface area which is the sum of the external and internal surface areas. Little is known about how the amount of total surface⁹⁷ available varies with particle size, type of coal, etc. Work is now proceeding on this subject at the U. S. Bureau of Mines by the method of obtaining low-temperature adsorption isotherms with argon.⁹⁸ Preliminary tests indicate that the total surface available for adsorption of this gas is 10 to 1,000 times greater than the external surface; the factor depends on the type of coal and the particle size.

In spite of the fact that gas-adsorption experiments⁹⁹ indicate that very large in-

vestigations, **3378** (1938), 6 pp., **3405**, (1938), 7 pp. Bangham, D. H., and Bennett, J. G., *Fuel*, **19**, 95-101 (1940).

⁹² Fischer, F., Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 184-7 (1933); *Fuel*, **12**, 394-7 (1933). Peters, K., and Picker, W., *Angew. Chem.*, **46**, 498-503 (1933). Peters, K., and Cremer, W., *ibid.*, **47**, 529-36. Smith, R. C., Tomarelli, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **61**, 2398-402 (1939).

⁹³ Tidswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **113**, 945-55 (1918), **115**, 895-902 (1919), **117**, 794-801 (1920), **127**, 125-32 (1925).

⁹⁴ Parr, S. W., and Coons, C. C., *Ind. Eng. Chem.*, **17**, 118-20 (1925).

⁹⁵ Coles, G., and Graham, J. I., *Fuel*, **7**, 21-7 (1928).

⁹⁶ Thiessen, R., *Ind. Eng. Chem.*, **24**, 1032-41 (1932). Agde, G., and Hubertus, R., *Braunkohlenarch.*, No. **46**, 3-30 (1936); *Fuel*, **16**, 288-303, 337-41, 366-75 (1937).

⁹⁷ Paneth, F., and Radu, A., *Ber.*, **57**, 1221-5 (1924). Rakovskii, E. V., Andreevskii, D. N., and Kunin, A. M., *Khim. Tverdogo Topliva*, **6**, 593-604 (1935); *Chem. Abs.*, **30**, 8566 (1936).

⁹⁸ Emmett, P. H., and Brunauer, S., *J. Am. Chem. Soc.*, **56**, 35-41 (1934), **59**, 310-5, 1553-64 (1937).

⁹⁹ Graham, J. I., *Trans. Inst. Mining Engrs.*, **52**, 338-47 (1916-17). Tidswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **113**, 945-55 (1918), **115**, 895-902 (1919), **117**, 794-801 (1920). Vondracek, R., and Hlavica, B., *Paliva a Topeni*, **9**, 2-12 (1927); *Chem. Abs.*, **22**, 3515 (1928). Eccles, A., Kay, H., and McCulloch, A., *J. Soc. Chem. Ind.*, **51**, 49-59T (1932). Agde, G., and Gözl, G., *Braunkohle*, **32**, 386-90 (1933). Coppens, L., *Ann. mines Belg.*, **37**, 173-219 (1936). Ruff, O., and Geselle, P., *Z. Berg- u. Hüttenw. deut. Reich*, **84**, 425-36

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ternal surface area is available to gases, oxygen does not penetrate far into coal. Examination and analysis of a large block of coal that had been exposed to air at room temperatures for 40 years showed only very slight oxidation of the coal 2 inches from the surface.¹⁰⁰ Outcrop coal that has been exposed to air for many thousands of years shows little evidence of oxidation when samples are taken more than 50 feet from the exposed part.¹⁰¹ Furthermore, permeability tests on thin sheets (3 millimeters) of solid coal have shown that extremely small amounts of gases (CH_4 , CO , CO_2 , H_2 , N_2 , and O_2) are forced through the sheet by pressure drops of 1 atmosphere across the sheet.¹⁰⁰

As a result of these considerations, it appears safe to assume for the present that ordinarily oxidation is merely a skin effect, but that this skin has a large internal surface area because of pores. The total surface area of these pores would be expected to be larger for coals of higher bed moisture content, which may explain the higher characteristic rate of oxidation of these coals. The rate of diffusion of oxygen into these small pores may affect the rate of oxidation, even at low temperatures.

The results shown in Fig. 6 and Table VI indicate that the measured characteristic rates of oxidation increase with the cube root of the external area of the coal particles. If no internal surface area were available by means of cracks, pores, and fissures, direct proportionality would be expected.

(1936); *Chem. Abs.*, **31**, 8155 (1937). Weiler, J. F., *J. Am. Chem. Soc.*, **58**, 1112-4 (1936). Syskov, K. I., and Ushakova, A. A., *Khim. Tverdogo Topliva*, **8**, 692-702 (1937); *Chem. Abs.*, **33**, 1908 (1939). Sinnatt, F. S., *Fuel*, **19**, 5-7, 38-42 (1940).

¹⁰⁰ Graham, J. I., *Trans. Inst. Mining Engrs.*, **58**, 32-9 (1919-20).

¹⁰¹ Porter, H. C., and Fieldner, A. C., *U. S. Bur. Mines, Tech. Paper* **35** (1914), 35 pp.

At high temperatures the rate of oxidation of the internal areas would become small relative to the rate of oxidation of the external area because of the slowness of diffusion of oxygen into the pores. In other words, at high temperatures the rate of oxidation would be expected to become proportional to the external area.⁵¹

METHODS OF MEASURING RELATIVE TENDENCIES TOWARD SPONTANEOUS IGNITION

A large number of methods using many different principles have been recommended for measuring the relative tendencies of various coals toward spontaneous ignition. A few of these methods will be discussed, and their more obvious advantages and disadvantages will be pointed out.

OBSERVATION OF STORAGE PILES OF VARIOUS COALS

The behavior of a coal when actually stored in large piles is, of course, the standard to which all laboratory methods must be referred. As a method of testing various coals, it has the decided advantage of directness and the disadvantages of high cost and poor control or essentially no control of the conditions of oxidation. As shown previously, the conditions of oxidation are extremely important. Small adventitious changes in conditions of oxidation in storage can easily outweigh any differences in characteristic rate of oxidation of various coals. Many experiments on large piles have been made (for the most part not published) that gave inconclusive results because either all the piles studied exhibited spontaneous ignition or else none of them did.

It is probable that all coals have been stored in large piles without the occurrence of spontaneous ignition and also that all coals have been known to ignite spontaneously. Table VIII illustrates the great im-

TABLE VIII

CHANGES IN CONDITIONS OF OXIDATION⁵⁸ REQUIRED TO CAUSE A THREE-FOLD INCREASE IN RATE OF OXIDATION OF TWO IDENTICAL COALS

Observed rate of oxidation	1	3
Temperature of oxidation	60° F	84° F
Size of coal particles	1-inch	18 mesh
		48 mesh
Oxygen in air	3.5 percent	20.9 percent
Time since oxidation started	Coarse coal 4 months	12 hours
	Fine coal 2.9 days	12 hours
Oxygen consumed, per-	Coarse coal 8.72	0.109
cent by weight of coal	Fine coal 0.909	0.477

portance of conditions of oxidation. It lists five different changes in conditions, each one sufficient to cause an approximate threefold increase in the observed rate of oxidation.⁵⁸ Figure 8 shows that a threefold range in characteristic rate of oxidation covers the field of ordinary commercial coking coals ranging from 18 to 40 percent volatile-matter content. A temperature rise in storage of only 24° F, for example, suffices to overcome the greatest difference in characteristic oxidation rate of these coals. As each of the four independent conditions (the last two items being essentially two aspects of the same factor) given in Table VIII triples the rate of oxidation of a coal, it can be seen that all the changes in conditions listed taken together could cause an 81-fold increase in rate of oxidation. This 81-fold change overshadows in importance the small difference between different coals.

The values in Table VIII are very approximate and are given merely to illustrate the need for directing research toward further studies of the effects of various conditions of oxidation on rates rather than giving attention exclusively to measurements of the relative oxidizabilities of various coals.

The disadvantage of poor control over conditions of oxidation in large-scale experiments in coal storage can be overcome,

at least partly, by the rather expensive method of studying the results of a large number of experiments, i.e., the statistical method.²

MEASUREMENTS OF RATES OF OXIDATION AT CONSTANT TEMPERATURES

This method^{45, 46, 102} of obtaining the relative tendencies of various coals to ignite spontaneously has been discussed at some length. The advantages are that: (1) conditions can be closely controlled; (2) conditions can be varied at will and singly; (3) results permit broad interpretations; and (4) samples of coal at various definite states of oxidation are made available for further tests. The disadvantages are that: (1) continuous operation of the apparatus is required for long periods of time; and (2) correlation of results with actual storage conditions is rather involved and indirect.

The first disadvantage listed can be avoided by the method of analyzing results described early in this chapter if characteristic rates of oxidation only are wanted, that is, if highly oxidized samples (of known values of X) are not required for further test. Only two accurate analyses of the effluent air from the apparatus taken at different times are required to locate a straight line, as shown in Fig. 1, and so determine the characteristic rate of oxidation of the sample. It is most interesting to note that, if the value of b is known or is calculated from the screen analysis of the coal sample, only one gas analysis is essential to determine the characteristic rate of oxidation. Furthermore, if a sample of coal to be tested has been exposed to an unknown amount of pre-

¹⁰² Francis, W., and Morris, H. M., *U. S. Bur. Mines, Bull.* **340** (1931), 44 pp. Stansfield, E., Lang, W. A., and Gilbert, K. C., *Am. Inst. Mining Met. Engrs., Contrib.* **69** (1934), 10 pp.; *Fuel*, **15**, 12-4 (1936).

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vious oxidation, this amount of oxidation and also the original characteristic rate of oxidation can be determined by merely taking two gas analyses of the effluent air. Substitution of the known or calculated value of b , the two measured rates of oxidation, and the known interval of time between gas analyses in equation 3 is all that is required.

The characteristic rate of oxidation of a coal is a measure of its tendency to ignite spontaneously. If conditions in the mine or storage pile are such that (1) sufficient air is available for the oxidation reaction and (2) the heat evolved on oxidation of the coal is not dissipated but serves to raise the temperature of the coal, the extremely high temperature coefficient of the oxidation reaction (Fig. 5) comes into play and the increased rate of oxidation in turn results in a further increase in temperature, and so on until the accelerating cycle brings the coal to a point near its decomposition temperature and the appearance of gas, fire, and flame soon follows.

Probably the chief reason why instances of spontaneous ignition are not more prevalent is the rapid decrease in rate of oxidation with increasing time or extent of oxidation. This factor has been covered rather thoroughly for the first time in the foregoing pages. When fresh coal is stored under ordinary conditions, a race, often close, sets in between the effects of the high temperature coefficient of the oxidation reaction, tending to promote spontaneous ignition, and the rapid decrease in rate of oxidation as oxygen is consumed. The winning effect determines whether or not spontaneous ignition occurs. If spontaneous ignition does not occur in the first 90 days of storage, it is fairly probable that it never will;² that is, the coal has become relatively "safe." It has been shown that the decrease in rate of oxidation with

time or extent of oxidation depends on particle size and is the same for all coals investigated. Consequently, it is the characteristic rate of oxidation of a coal that determines primarily whether or not spontaneous ignition occurs.

In the above discussion the rate of heat loss has not been considered. It is a variable depending more upon the height of the storage pile and amount of ventilation than upon any property of the coal. Of course, the moisture content of the coal may affect the rate of heat loss and effective specific heat of the coal because of the evaporative effect.⁴⁶

Experiments have shown that, as would be expected, the rate at which heat is developed by the oxidation is proportional to the rate of oxidation.¹⁰³ Lamplough and Hill¹⁰⁴ reported the heat evolved in the low-temperature oxidation of coal as 3.3 calories per cubic centimeter (N.T.P.) of oxygen consumed. Winmill⁴⁶ measured the rate of temperature rise in an adiabatic calorimeter when coal was oxidized at 40 to 55° C and found a value of 2.1 calories per cubic centimeter of oxygen consumed. He also pointed out some reasons why the results of Lamplough and Hill may be too high. Two and one-tenth calories per cubic centimeter of oxygen used corresponds to 1,470 calories per gram of oxygen used, which is about 90 percent of the heat that would be evolved if the oxygen went entirely to the formation of carbon monoxide. Much information on spontaneous ignition can be obtained by utilizing these values¹⁰⁵ and the rate of oxidation of a

¹⁰³ Davis, J. D., and Byrne, J. F., *Ind. Eng. Chem.*, **17**, 125-30 (1925).

¹⁰⁴ Lamplough, F. E., and Hill, A. M., *Trans. Inst. Mining Engrs.*, **45**, 629-57 (1912-13).

¹⁰⁵ Scott, G. S., *U. S. Bur. Mines, Circ. 7053* (1939), 10 pp. Scott, G. S., Jones, G. W., and Cooper, H. M., *Ind. Eng. Chem.*, **31**, 1025-7 (1939).

coal to calculate the rate of temperature rise under various conditions.⁴⁶

MEASUREMENTS OF RATES OF TEMPERATURE
RISE OF COAL SAMPLES WHEN EXPOSED
TO AIR OR OXYGEN

Considerable ingenuity has been exercised in devising methods to demonstrate and study the phenomenon of spontaneous ignition in laboratory-scale equipment. It is difficult to set conditions just right so that the self-heating effect of small coal samples is large enough to give precise and reproducible results. As will be seen later, the expedients that are often employed to magnify the small, self-heating effects sometimes subject a method to serious objections.

In general, measuring the rate of temperature rise of small samples exposed to oxygen or air has the decided advantage of being the most direct laboratory-scale method for measuring the relative tendencies of various coals toward spontaneous ignition in storage piles. It obviates, at least partly, all measurements of the various factors that have just been discussed at length, such as the characteristic rate of oxidation, the effect of time or extent of oxidation on rate, the amount of heat developed per unit of oxygen consumed, and the effective specific heat of the coal. In fact, the method requires essentially only one measurement—the rate of temperature rise of the coal. Another advantage is that tests are completed in a very short time, sometimes requiring less than an hour.

One general disadvantage of the method is that because of its very directness the results are not subject to very wide interpretation; that is, they often apply only to the phenomenon of spontaneous ignition, although sometimes they are of interest in combustion studies. No samples of coal at definite stages of oxidation are made

available for further tests for changed properties.

It is the relative rate of self-heating of various coals at low temperatures, say from 30 to 100° C, that is of particular interest in studies of spontaneous ignition in storage piles. As stated early in the chapter, experience with storage piles has shown that, if the temperature of the pile rises by self-heating to 80 or 100° C, spontaneous ignition is practically assured anyway,^{2, 43, 83} and so the rate of rise from 80 to the ignition point (200° C) has less direct practical significance.

To obtain a measurable amount of self-heating in small samples in the temperature range 30 to 100° C, the rate of heat loss from the sample must be kept very near zero. Winnill⁴⁶ obtained this result by exposing to oxygen a rather large sample (250 grams) in a vacuum bottle immersed in a bath, the temperature of which was raised at the same rate as the coal; that is, the temperature difference, coal to bath, was kept near zero. His results, put upon an absolute basis by suitable calibration of the instrument, have already been discussed.

Davis and Byrne¹⁰³ devised the adiabatic apparatus shown in Fig. 9. A 24-element thermocouple connected to galvanometer *g* actuated photoelectric cell *i*, which, through a suitable system of relays, heated oil bath *a* at the same rate as the coal sample in *b* heated itself by oxidation.

Results were reported on seven coals and a peat sample when exposed to oxygen at 70° C. Illinois coal (volatile matter 37.2 percent, oxygen 11.6 percent) showed the highest rate of rise in temperature, heating from 70 to 100° C in 5.1 hours. Upper Kittanning Seam coal (volatile matter 19.5 percent, oxygen 2.8 percent) showed the lowest (except anthracite) rate, requiring 14 hours for the same rise in temperature.

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Samples of anthracite, Pocahontas Seam coal, and peat did not exhibit self-heating when exposed to oxygen at 70° C in these experiments.

A similar apparatus¹⁰⁶ used to measure the effect of small amounts of oil such as are employed for dust-prevention treat-

thorough investigation of the effects of various factors on the results obtained in an adiabatic calorimeter.¹¹¹

A great number of tests by methods where the rate of heat loss from the sample is not kept near zero have been reported. Relative values of the tendency for spon-

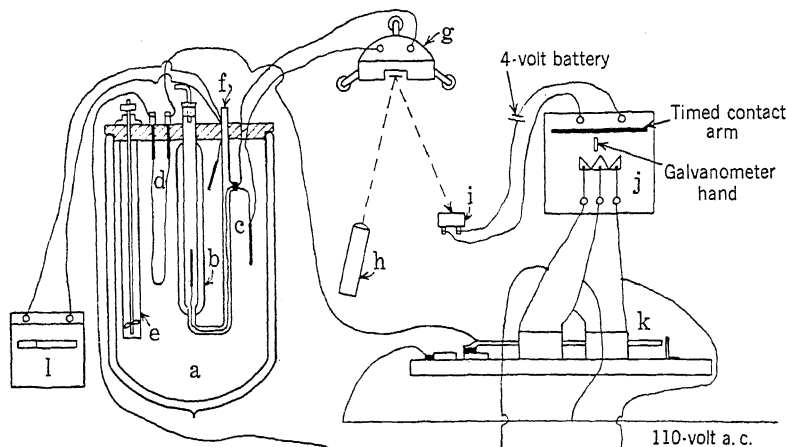


FIG. 9. Adiabatic apparatus for measuring self-heating of coal in oxygen.¹⁰³

ments of fuel¹⁰⁷ showed that oil does not increase the tendency for spontaneous ignition.¹⁰⁸

Japanese workers, employing the adiabatic method,¹⁰⁹ have reported results on 75 coals.¹¹⁰

Makarov and Oreshko have made a

¹⁰⁶ Weinrich, W., and Gaspari, H. J. R., *Ind. Eng. Chem., Anal. Ed.*, **8**, 307-10 (1936).

¹⁰⁷ Schmidt, L. D., *U. S. Bur. Mines, Circ.* **6932** (1937), 10 pp.

¹⁰⁸ Mott, R. A., and Wheeler, R. V., *Colliery Guardian*, **147**, 483-6 (1933). West, C. E., *Coal Age*, **41**, 229-30 (1936). Ambrose, H. A., and Gaspari, H. J. R., *ibid.*, **42**, 252-4 (1937); *Power*, **81**, No. 7, 378-80 (1937). Pilcher, J. M., and Sherman, R. A., *Bituminous Coal Research, Inc., Tech. Rept.* **6** (1939), 36 pp.

¹⁰⁹ Inaba, J., Miyagawa, I., and Yamada, M., *Bul. Sci. Fakultat. Terkultura, Kjusu Imp. Univ.*, **3**, 210-17 (1928); *Chem. Abs.*, **23**, 2270 (1929).

¹¹⁰ Miyagawa, I., Yamada, M., and Inaba, J., *J. Fuel Soc. Japan*, **8**, 776-880 (1929); *Chem. Abs.*, **23**, 5299 (1929).

taneous ignition of various coals can be obtained in this way if the rate of heat loss is not too large and uncertain. Parr and Kressman¹¹² obtained measurable self-heating effects at low temperatures by using large samples. From 35 to 40 pounds of coal was placed in 5-gallon jars with perforated bottoms, and these jars were exposed to air in ovens maintained at constant temperatures of 40, 60, 80, and 115° C.

Dennstedt and Büinz¹¹³ passed oxygen at the rate of 2 or 3 liters an hour through

¹¹¹ Makarov, S. Z., and Oreshko, V. F., *Bull. acad. sci. U.R.S.S., Class Sci. Tech.*, No. **2**, 49-60 (1940), No. **3**, 35-42 (1940), No. **8**, 99-112 (1940); *Chem. Abs.*, **35**, 8297, 8298 (1941), **36**, 1464 (1942).

¹¹² Parr, S. W., and Kressman, F. W., *Univ. Illinois Eng. Exp. Sta., Bull.* **46**, (1910), 87 pp.

¹¹³ Dennstedt, M., and Büinz, R., *Z. angew. Chem.*, **21**, 1825-35 (1908).

coal at constant temperatures of 135 and 150° C; they classified coals as follows: (1) those in which the temperature of the coal did not exceed that of the oil bath at either 135 or 150° C and which are safe for storage and transportation; (2) those which, after treating 2 hours at 135° C then raising to 150° C, showed temperature rise or perhaps ignition; (3) those in which the temperature of the coal increased only slightly but which could be caused to heat strongly by increasing the supply of oxygen and which are dangerous for storage; and (4) those which heated rapidly and ignited within 2 hours, and which are the most dangerous for storage and transport.

IGNITION AND CROSSING-POINT METHODS AS MEASURES OF RELATIVE TENDENCY FOR SPONTANEOUS IGNITION

In these methods the temperature of the bath is raised in a prescribed manner, thus raising the temperature of the coal through which oxygen or air is passed.¹¹⁴ The rate of oxidation of the coal increases until it is rapid enough for the coal to self-heat at a rate greater than the rate of temperature rise of the bath. At this point, the crossing point, the temperature of the coal becomes equal to that of the bath momentarily, and then usually the coal temperature increases rapidly and the appearance of fumes, glowing, and ignition soon fol-

low.¹¹⁵ Reported values of ignition points, glow points,¹¹⁶ and kindling temperatures, etc., range from 20° C for peat char¹¹⁷ to 600° C for coke,¹¹⁸ with many bituminous coals reported at 150 to 250° C. The values obtained depend on the particular apparatus and the conditions.^{59, 119}

The work of Sebastian and Mayers¹²⁰ shows that a modification of the usual method of determining the crossing-point temperature is very satisfactory for the characterization of fuels. Preoxidation raises the crossing-point temperature.^{59, 121} Exhaustive preoxidation in one instance raised the temperature of ignition of a coal from 120 to above 350° C.¹²²

RATES OF OXIDATION IN AQUEOUS SOLUTIONS OF CHEMICAL OXIDIZING AGENTS

This method for measuring the relative tendencies of various coals towards spontaneous ignition has the advantage that: (1) only small samples are required and (2) tests are completed in a short time. The most obvious disadvantage is that con-

¹¹⁴ Wheeler, R. V., *J. Chem. Soc.*, **113**, 945-55 (1918). Dunoyer, L., *Chaleur ind.*, **9**, 43-53 (1928). Kreulen, D. J. W., *Brennstoff-Chem.*, **11**, 261-2 (1930), **12**, 107-11 (1931). Agde, G., and Götz, G., *Braunkohle*, **32**, 386-90 (1933). Sustmann, H., and Lehnert, R., *Brennstoff-Chem.*, **19**, 21-7 (1938). Voitova, E. V., and Zamyatina, L. A., *Khim. Tverdogo Topliva*, **9**, 85-91 (1938); *Chem. Abs.*, **32**, 6431 (1938). Nelson, H. W., Brysch, O. P., and Lum, J. H., *Fuel*, **18**, 42-55, 85-91 (1939). Seyler, C. A., and Jenkins, T. E., *Symposium on Combustion of Solid Fuels*, Am. Chem. Soc., Boston, Sept. 12, 1939, pp. 18-27; *Chem. Abs.*, **34**, 6432 (1940). Porter, H. C., *Ind. Eng. Chem.*, **32**, 1034-6 (1940).

¹¹⁵ Peters, K., and Picker, W., *Angew. Chem.*, **46**, 498-503 (1933). Peters, K., and Cremer, W., *ibid.*, **47**, 529-36 (1934). Bunte, K., Brückner, H., and Bender, W., ref. 59.

¹¹⁶ Sinnatt, F. S., and Moore, B., *J. Soc. Chem. Ind.*, **39**, 72-ST (1920). Moore, B., *Fuel*, **11**, 267-73 (1932).

¹¹⁷ Gavrilov, N. N., and Veisburg, L. A., *Khim. Tverdogo Topliva*, **2**, No. 8, 41-54 (1931); *Chem. Abs.*, **28**, 5960 (1934).

¹¹⁸ Winter, H., and Mönnig, H., *Glückauf*, **74**, 335-6 (1938).

¹¹⁹ Steinbrecher, H., *Braunkohle*, **27**, 101-8 (1928). Gärtner, K., *Mathematik, Természettud. Értesítő Magyar Tudományos Akad. III Osztályának Folyóirata*, **46**, 378-408 (1929); *Chem. Abs.*, **25**, 2834 (1931). Hartgen, F. A., and Smith, D. F., *U. S. Bur. Mines, Rept. Investigations*, **2960** (1929), 5 pp.

¹²⁰ Sebastian, J. J. S., and Mayers, M. A., *Ind. Eng. Chem.*, **29**, 1118-24 (1937).

¹²¹ Parr, S. W., and Coons, C. C., *Ind. Eng. Chem.*, **17**, 119-20 (1925).

¹²² Fischer, F., Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 184-7 (1933); *Fuel*, **12**, 394-7 (1933). Cf. Rees, O. W., and Wagner, W. F., *Ind. Eng. Chem.*, **35**, 346-8 (1943).

ditions differ so greatly from atmospheric oxidation in storage that interpretation of the results is difficult. The factor of difference in wettability of the surface of various coals may have an appreciable influence on the results. A great many coals have been tested by this method,^{110, 123} and rates of oxidation increase regularly with decreasing rank of coal.⁶⁰

EFFECT OF OXIDATION ON PROPERTIES OF COAL

Perhaps it is not too obvious to mention that the most serious change that can take place in coal on storage occurs when the pile fires spontaneously and the coal burns to ashes. Barring this unfortunate occurrence, the next most serious change is the loss in coking power of coking coals, which is of great industrial importance.

CHANGES IN CARBONIZING PROPERTIES OF COKING COALS CAUSED BY ATMOSPHERIC OXIDATION

In general, when crushed coking coals are heated above their decomposition temperature in the coke oven the original particles of coal fuse into coherent blocks of coke. No traces remain of the identifying outlines of the original pieces of coal. This ability to fuse may be destroyed completely by

storage in air even though no serious heating occurs in the coal pile. If, in this extreme case, the oxidized coal were carbonized under conditions prevailing in ordinary commercial coke ovens it would come out as loose char, the individual pieces closely resembling the pieces of coal that entered the oven.

A rather extensive series of tests has been made recently at the U. S. Bureau of Mines on change in coking properties with oxidation.¹²⁴ Figure 10 shows a picture of the apparatus that was designed and built for the controlled oxidation of 182-kilogram samples of 0 to 1/4-inch coal.⁴⁵ The double-jacketed drum is half filled with coal and rotated slowly while air is passed over the coal at a measured rate. Water boiling in the outside jacket maintains the coal at 99.3° C. The amount of oxygen consumed by the coal is measured by gas analyses of the effluent air. The sources, analyses, and characteristic rates of oxidation at 99.3° C for nine of the coals tested are shown in Table VII and Fig. 8. Periodically samples of oxidized coal were taken from the drum for analysis and carbonization. Representative samples (80 kilograms) were carbonized in cylindrical mild-steel retorts (diameter, 46 centimeters) in a furnace maintained at 800° C. The physical and chemical properties of the coke and by-products were determined by standard methods.¹²⁵ Pictures of typical pieces of coke made from each oxidized coal are shown in the series of technical papers of the U. S. Bureau of Mines covering the carbonizing properties of these coals.¹²⁶

¹²⁴ Schmidt, L. D., Elder, J. L., and Davis, J. D., *Ind. Eng. Chem.*, **32**, 548-55 (1940).

¹²⁵ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph 5* (1934), 164 pp.

¹²⁶ Fieldner, A. C., et al., *U. S. Bur. Mines, Tech. Papers 594* (1939), 43 pp., **596** (1939), 46 pp., **599** (1939), 38 pp., **601** (1939), 45 pp., **604** (1940), 65 pp., **616** (1941), 47 pp., **621** (1941), 77 pp.

¹²³ Kreulen, D. J. W., *Brennstoff-Chem.*, **10**, 397-400 (1929). Francis, W., *Fuel*, **12**, 128-38 (1933). Ermolenko, N. F., and Ginzburg, D. Z., *Belaruskaya Akad. Navuk, Inst. Khim. Sbornik Prats.*, **1**, 143-64 (1934); *Chem. Abs.*, **31**, 2780 (1937). Pieters, H. A. J., and Koopmans, H., *Het Gas*, **54**, 71-82, 93-8 (1934). Gauzelin, M., and Crussard, L., *Rev. ind. minérale*, **1**, 373-402 (1937); *Fuel*, **17**, 19-27 (1938). Lowry, H. H., *J. Inst. Fuel*, **10**, 291-301 (1937). Balfour, A. E., Blayden, H. E., Carter, A. H., and Riley, H. L., *J. Soc. Chem. Ind.*, **57**, 1-7 (1938). Francis, W., *Fuel*, **17**, 363-72 (1938). Niyogi, B. B., *Fuel*, **17**, 228-9 (1938); *Chem. Abs.*, **32**, 8743 (1938). Morrison, G. K., *J. Chem. Met. Mining Soc. S. Africa*, **40**, 201-12 (1939), 237-40 (1940); *Bull. Fuel Research Inst. (S. Africa)*, **17** (1940), 12 pp.

CHANGES IN CARBONIZING PROPERTIES OF COKING COALS

Figure 11 shows the effects of oxidation of coal from the Pocahontas No. 3 Seam (coal No. 56). Piece *A* was made from fresh coal; *B* was made from coal that had been oxidized for 4 days in air at 99.3° C and had consumed 0.55 gram of oxygen per 100 grams of pure coal; *C* was made from coal that had been oxidized for 11.8 days

oxidation, but there is general deterioration in strength of coke.

The strength of coke, at least up to a certain ill-defined point, is commonly used as a criterion of its value for specific purposes, such as for the foundry and blast furnace. In Fig. 12,⁵⁸ the coke-strength index¹²⁷ for each coal is plotted against the

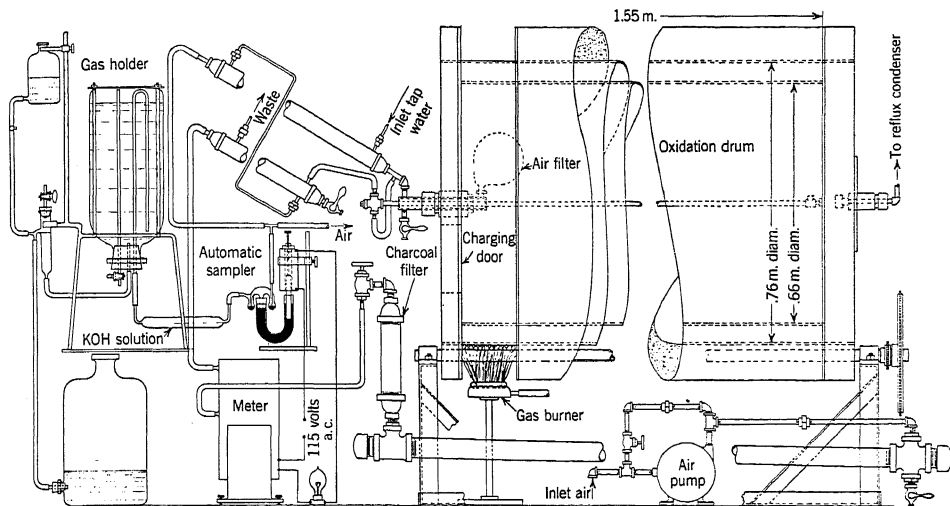


FIG. 10. Apparatus for controlled oxidation of coal.⁴⁵

and had consumed 1.33 grams of oxygen per 100 grams of pure coal. The first visual evidence of oxidation of the coal was a finer cell structure in the coke, accompanied by an increase in the apparent specific gravity of the coke. Further oxidation of the coal resulted in the formation of loose char in the entire central portion of the charge where the rate of heating was lowest. At this advanced stage the shell of coherent coke (*C*, Fig. 11) that was formed in the zone of high heating rate near the outside of the retort was of low strength and "pebbly." In general, poor fusion is especially pronounced with low-volatile coals; with high-volatile coals the tendency is for fusion to stay good with increasing

amount of oxygen that has been consumed by the coal. The numerals spaced along each curve in this figure indicate the number of days' oxidation in air (20.93 percent oxygen) at 99.3° C. The closer the numerals are spaced, of course, the lower the characteristic rate of oxidation of the coal.

Low-oxygen coals of the high- and medium-volatile content category in general are relatively insensitive to oxidation. The coke-strength index remains fairly constant for a while, even rising some-

¹²⁷ Coke-strength index = 0.225 (1.5-inch shatter) + 0.293 ($\frac{1}{4}$ -inch tumbler) + 0.352 (1-inch tumbler) + 0.202 (percentage of coke from the retort retained on a 1-inch screen) + 0.408 (100 - friability). The coke-strength indexes of all nine coals from fresh coal are adjusted to average 100.

what,^{128, 129} and then falls rapidly with increasing oxidation. Coal 54 is a high-volatile coal, but the oxygen content of the fresh coal is exceptionally high for a coking coal. Its coking power is very sensitive to

Figure 12 can be used as a master chart to find for each coal the amount of oxygen required to reduce the coke strength index by 15 percent. This value is represented by symbol, X_{15} , which is a characteristic

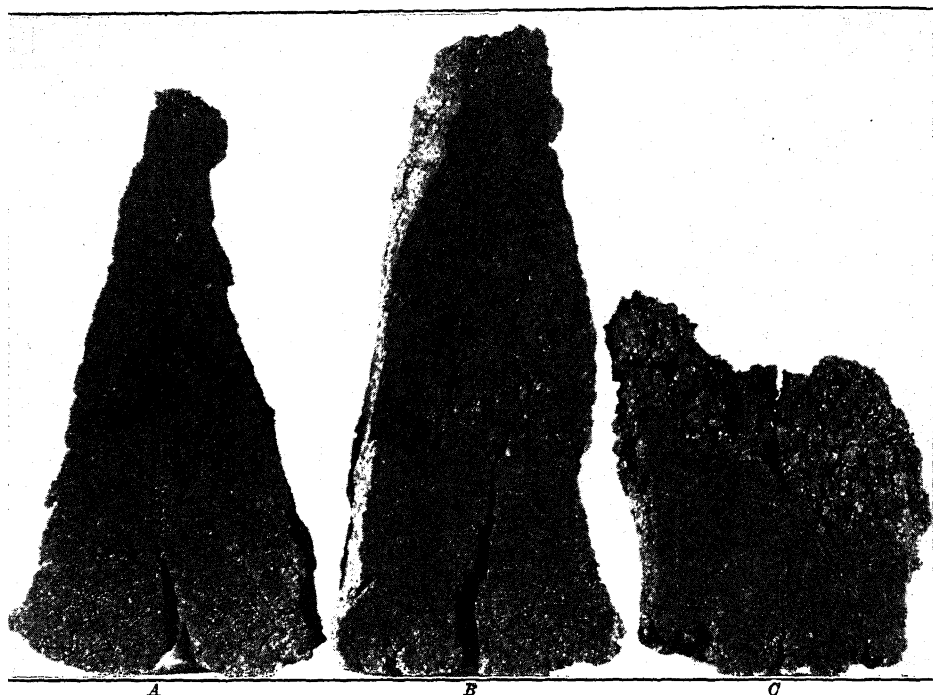


FIG. 11. Effect of oxidation of Pocahontas No. 3 Seam coal on the structure of coke produced from it.¹²⁰

- A. Coke from unoxidized coal.
- B. Coke from coal oxidized 4 days in air at 99.3° C.
- C. Coke from coal oxidized 11.8 days in air at 99.3° C.

oxidation. Coals 56 and 57 are in the low-volatile classification, and their coking power also is relatively sensitive to oxidation.

¹²⁸ Koppers, H. H., *Fuel*, **12**, 52-65 (1933).
Agde, G., and Winter, A., *Brennstoff-Chem.*, **15**, 46-50, 64-8 (1934).

¹²⁹ Schmidt, L. D., Elder, J. L., and Davis, J. D., *Ind. Eng. Chem.*, **28**, 1346-53 (1936); *Fuel*, **16**, 39-48 (1937); *Glückauf*, **73**, 804-6 (1937).
Price, J. D., *Iron Steel Engr.*, **18**, No. 3, 71-2 (1941).

value for each coal and is an inverse measure of the sensitivity of the coking power of the coal to oxidation. Figure 13 shows an empirical way of plotting this value for each coal against the volatile-matter (V_o), and oxygen (O_o), contents of coal.⁵⁸ The points fall fairly well along a straight line.

The sensitivity of a new coal can be predicted from its analysis by merely substituting in the equation given on Fig. 13 the percentage volatile matter and oxygen in

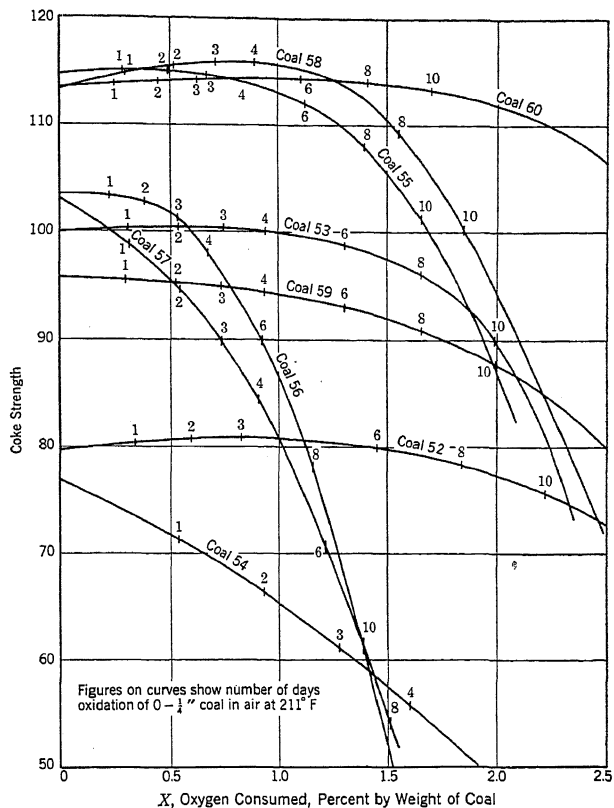


FIG. 12. Coke strength index as a function of the amount of oxygen consumed by the coal.⁵⁸

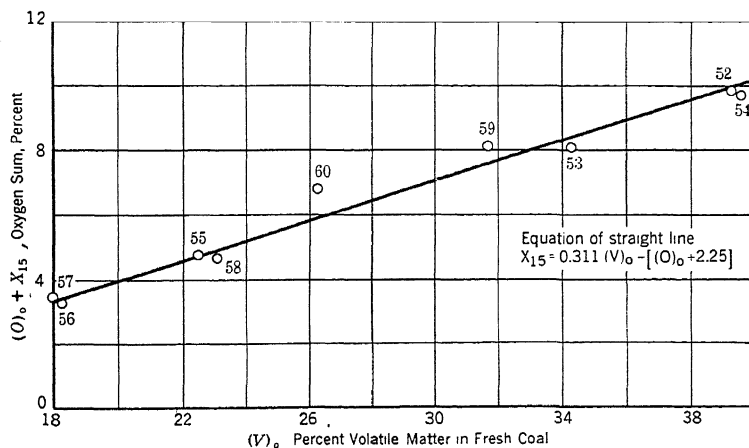


FIG. 13. The relation of volatile matter in fresh coal to the sum of the oxygen in the fresh coal plus that necessary to reduce the coke strength index by 15 percent.¹²⁹

the fresh coal, or the sensitivity of a coal can be estimated graphically from Fig. 13. For example, Pittsburgh Seam coal 52, with an original oxygen content for fresh coal of 7.0 percent, can consume 2.8 percent oxygen before its oxygen sum is up to the line value of 9.8 and the coke-strength index is decreased by 15 percent. In contrast, fresh High Splint Seam coal 54 of about the same volatile matter content has a relatively high oxygen content of 8.7 percent, so that it can consume 1 percent oxygen before its oxygen sum is up to the line and its coke-strength index is decreased by 15 percent.

These results indicate that coals of high original oxygen content not only consume oxygen at a relatively high rate (Fig. 8), but also that their coking power is destroyed by relatively little oxygen. The slope of the line in Fig. 13 shows that, the higher the volatile-matter content of a coal, the higher the original oxygen content can be and the coal still have good coking and storing qualities.

Figures 8 and 13 can be used for making rough predictions of the relative storing properties of coking coals from the proximate and ultimate analyses of the fresh coals. Unfortunately, an important factor in this prediction is the percentage oxygen content of the fresh coal. Customarily this value is obtained by difference in the ultimate analysis and so is subject to relatively large experimental error. It is apparent that the percentage oxygen in coals is a most important factor, and any efforts devoted to further development and more prevalent usage of accurate methods for the direct determination of oxygen¹³⁰ would be very much worth while.

¹³⁰ Kirner, W. R., *Ind. Eng. Chem., Anal. Ed.*, **6**, 358-63 (1934), **8**, 57-61 (1936).

EFFECT OF OXIDATION ON YIELDS OF CARBONIZATION PRODUCTS

Table IX shows for the nine coals described in Table VII the effect of oxidation on the yields of carbonization products.⁵⁸ The first three columns show the yields from fresh coal in kilograms per 100 kilograms of dry, ash-free coal, and the last three columns the percentage change in these yields when each coal is oxidized just

TABLE IX

SUMMARY OF EFFECTS OF OXIDATION ON CARBONIZATION YIELDS—AVERAGE CARBONIZATION YIELDS OF NINE COALS

Material	Values for Fresh Coal			Change Caused by Oxidation *		
	Range from		Ave.	Range from		Ave
	High-Vola- tile	Low-Vola- tile		High-Vola- tile	Low-Vola- tile	
	percent			percent		
Coke	65.1	84.7	75.8	+3.5	-0.22	+1.15
Tar †	9.7	2.0	5.5	-39.0	-15	-33.4
Gas	17.9	10.9	13.5	+9.1	-0.5	+4.1
Thermal yield in gas, calories per gram of pure coal	1,860	1,480	1,672	Irregular		-2.6
Ammonia	Constant		0.289	Irregular		+0.0
Liquor	4.9	1.3	3.0	Irregular		+27.1
Light oil	1.2	0.5	0.8	Irregular		+5.3

* Each coal oxidized just enough to cause a 15 percent decrease in the coke-strength index.

† Excluding High Splint Seam coal 54.

enough to cause a 15 percent decrease in its coke-strength index. These percentage changes in yield represent about the maximum changes that would be expected in commercial byproduct ovens from use of stored coal.

The yields of tar decrease rapidly with oxidation of the coal, showing, on an average, a 33.4 percent decrease from the value for fresh coal, when the coals have been oxidized just enough to cause a 15 percent decrease in coke-strength index. This rapid decrease in yield of tar with oxidation

makes an excellent measure of the extent of the oxidation. Incidentally, it is interesting to note that the tar yields obtained from Pittsburgh Seam coal oxidized at three different temperatures indicate that the temperature of oxidation in the range 30 to 100° C is of minor importance. For 1 percent oxygen consumed ($X = 1$) the yield of tar decreased by 14, 13, and 16 percent, respectively, for oxidation at 30, 50, and 99.3° C.¹²⁴

The average yield of gas from oxidized coals is 4.1 percent higher, as shown in Table IX. Gas analyses showed that this increase is due almost entirely to carbon dioxide and carbon monoxide. The heating value of the gas per unit weight of pure coal shows a 2.6 percent decrease upon oxidation.

The increased yield of ammonia from oxidized coal may be associated with the increase in yield of liquor. In the carbonization process the presence of steam protects ammonia from decomposition.¹³¹

The detailed analyses of tar, coke, and light oil did not change greatly with the amount of oxidation to which these coals were subjected. For example, the analysis of coke, including the percentage of sulfur, did not change appreciably with oxidation of the coal.

Thiessen¹³² also found that the sulfur content of cokes did not decrease as much as expected when pyrites were oxidized before carbonization. The iron compounds from the oxidized pyrites increase the retention of sulfur in the coke.

Donnelly and others⁸⁴ carbonized small samples of oxidized coals at 600° C and made precise measurements of the yields.

When the coal had consumed 47 percent of its weight of oxygen, the yield of tar had decreased from 17.0 percent for fresh coal to 3.2 percent; the yield of coke had increased from 77.2 to 79.8 percent, and the yield of gas had increased from 2.7 percent for fresh coal to 17.5 percent.

Bhattacharjee and Dutta-Roy¹³³ found that the yield of tar on carbonization proved to be the best method for differentiating oxidized coal from fresh coals. Jamieson and others³⁵ found that upon storing coals the coking properties were affected before there was any appreciable change in other properties. They found also that stored coal when carbonized in vertical retorts gave an increased thermal yield in the gas. This effect may have been caused by increased water-gas reaction connected with the increase in yield of liquor.

Kattwinkel¹³⁴ oxidized three coking coals for 90 days in a steam drying oven at 80° C. The coking power was destroyed completely. The effect on other carbonizing properties is shown in Table X.

TABLE X

EFFECT OF OXIDATION UPON CARBONIZATION PROPERTIES OF THREE WESTPHALIAN COALS¹³⁴

Coal No.	1	2	3
Volatile-matter content of fresh coal	31.3	26.3	20.3
Increase in oxygen content (percent of coal)	6.0	6.2	2.9
Increase in weight of coal (percent of coal)	3.5	2.9	1.8
Change in yield of tar (percent of value for fresh coal)	-73.8	-70.3	-71.2
Change in yield of gas	-17.1	-0.9	-2.8
Change in yield of ammonia (percent of value for fresh coal)	+18.1	+10.7	+6.0
Change in yield of benzol (percent of value for fresh coal)	-49.3	-27.6	-21.8

¹³¹ Porter, H. C., *Coal Carbonization*, Chemical Catalog Co., New York, 1924, p. 83.

¹³² Thiessen, G., *Ind. Eng. Chem.*, **27**, 473-8 (1935); *Fuel*, **16**, 352-8 (1937).

¹³³ Bhattacharjee, R. C., and Dutta-Roy, R. K., *Quart. J. Geol. Mining Met. Soc. India*, **7**, 169-80 (1935); *Chem. Abs.*, **31**, 3668 (1937).

¹³⁴ Kattwinkel, R., *Glückauf*, **63**, 160-5 (1927).

USE OF PREOXIDIZED COKING COALS

In general, the oxidation of coking coals results in decreased value or deterioration. However, in some coals a limited amount of oxidation results in stronger coke.^{128, 129} Coals are sometimes deliberately preoxidized to obtain special plastic properties such as decreased "stickiness"¹³⁵ or fluidity¹³⁶ or to change the characteristics of the mix going to the coke oven. Coke-oven tests have shown that fine coal weathered for several months to a year could replace part of the low-volatile coal used for blending.¹³⁷ Excessive expansion in the coke oven can be controlled by preheating or preoxidation, often at the cost of lowered coke strength.¹³⁸ Many patents have been issued for methods of obtaining certain desired changes in coking characteristics by preoxidation.

Durain, coked after strong preoxidation, can be converted to highly activated carbon.¹³⁹

CHANGE IN AGGLUTINATING VALUE WITH OXIDATION

The agglutinating value¹⁴⁰ is reported as the crushing strength, in kilograms, of pellets made by carbonizing a small charge containing 15 parts by weight of sand or silicon carbide to 1 part of powdered coal.

¹³⁵ Leshner, C. E., and Zimmerman, R. E., *Coal Age*, **44**, No. 3, 45-9 (1939); *Trans. Am. Inst. Mining Met. Engrs.*, **139**, 328-63 (1940).

¹³⁶ Jäppelt, A., and Steinmann, A., *Oel u. Kohle*, **13**, 1027-30 (1937). Steinmann, A., *Braunkohlenarch.*, No. 49-50, 3-29 (1938).

¹³⁷ Michaelis, P., *Glückauf*, **71**, 413-23 (1935). Sapozhnikov, L. M., *Coal Carbonisation*, **3**, 42-4, 95-7 (1937).

¹³⁸ Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 445-50 (1933). Ipfelkofer, J., *Gas- u. Wasserfach*, **83**, 217-21, 233-6 (1940).

¹³⁹ Lambris, G., and Boll, H., *Brennstoff-Chem.*, **19**, 177-84 (1938).

¹⁴⁰ *Proc. Am. Soc. Testing Materials*, **34**, Pt. I, pp. 457-62 (1934). *Am. Soc. Testing Materials, Tentative Standards*, 1938, Pt. II, Non-Metals, 95-100.

The agglutinating value provides one of the best criteria of the extent of oxidation of stored coking coals.¹⁴¹ Although not the most sensitive indication of extent of oxidation, it has the decided advantage that it measures a property of coal closely related to coking power. In Fig. 14 the agglutinating values of the coking coals described in Table VII are shown plotted against the extent of oxidation.¹²⁴ Unless otherwise indicated, the values are for coal oxidized in the zero to ¼-inch size in air at 99.3° C. It will be noted that in most instances the agglutinating values decrease at an accelerating rate as oxidation progresses. A short, vertical line is drawn on each curve at the point where oxidation had caused a 15 percent decrease in the coke-strength index. On the average of nine coals, a 34 percent decrease in agglutinating value resulted in a 15 percent decrease in coke-strength index, and no single coal deviated very significantly from this average behavior. In other words, for most of the coals taken singly, a 34 percent decrease in agglutinating value resulted in roughly a 15 percent decrease in coke-strength index.

Among the ways that operators of coke plants can compensate for the effect of oxidation of stored coals are: (1) by increasing the percentage of low-volatile coal in the mix, (2) by mixing increased amounts of fresh coal with the stored coal going to the ovens, or (3) by increasing oven temperature. The agglutinating-value test should be of assistance to operators in making appropriate changes to compensate for oxidized coal.⁵⁶ The exact method of utilizing agglutinating values for this purpose must be determined by the

¹⁴¹ Barash, M., *J. Soc. Chem. Ind.*, **48**, 174-183T (1929). Marshall, S. M., Yancey, H. F., and Richardson, A. C., *Trans. Am. Inst. Mining Met. Engrs.*, **88**, 389-93 (1940). Agde, G., and Winter, A., *Brennstoff-Chem.*, **15**, 46-50 (1934).

operator by correlation with experience under the particular conditions of operation.

Finney has reported that, with some high-volatile coals, difficulties occur in pushing coke from the ovens before oxidation is extensive enough to affect the agglutinating value materially.¹⁴² A more sensitive test for oxidation of the coal would help operators to minimize operating troubles and aid in producing better coke.¹⁴³

extent of oxidation.¹⁴⁵ Kucherenko¹⁴⁵ found that swelling pressure at constant volume was a much more sensitive measure of extent of oxidation than was the agglutinating value and that it correlated well with the decrease in thickness of the plastic layer caused by increasing oxidation.

CHANGES IN PROXIMATE AND ULTIMATE ANALYSIS CAUSED BY OXIDATION

Study of the changes in proximate and ultimate analysis caused by progressive

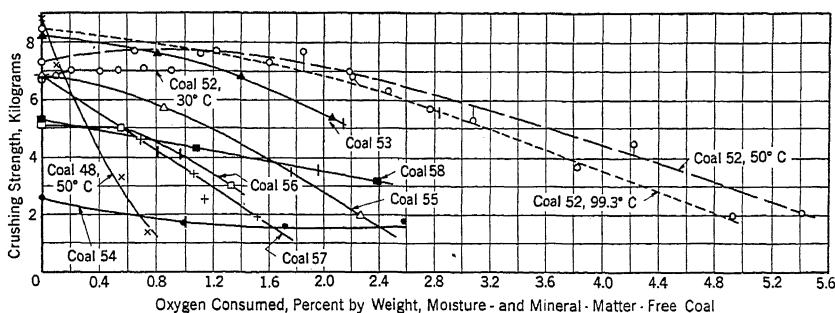


FIG. 14. Agglutinating values of American coals as a function of extent of oxidation.¹²⁴

Boll¹⁴⁴ reported that a method for measuring expansion pressure proved to be much more sensitive to oxidation than the agglutinating value. A few tenths of 1 percent oxygen consumed reduced this value to zero, whereas the agglutinating value was strongly influenced only after 2 percent oxygen had been added. The free expansion did not decrease appreciably until 0.5 to 2.0 percent oxygen had been added. Addition of small amounts of sulfur, selenium, and boric acid had much the same effect on these tests as oxygen. Other measures of the plastic properties of coal have also proved to be sensitive to the

oxidation of the nine coking coals in Table VII showed that the heating value and percentage carbon content of the samples decreased linearly with increasing extent of oxidation (X), while the percentage oxygen in the coal increased linearly.¹²⁴ Table XI indicates the extent of these changes when the average coal has consumed 1 gram of oxygen per 100 grams of pure coal.⁵⁸

Probably the best single measure of extent of oxidation among these changes is the 0.69 percent decrease in heating value. It should be noted that these

¹⁴² Finney, D. P., *Iron Steel Engr.*, **18**, No. 3, 70 (1931).

¹⁴³ Hagedorn, F. A., *ibid.*, **18**, No. 3, 70-1 (1941).

¹⁴⁴ Boll, H., dissertation, Aachen, 1933, 29 pp.; *Gas- u. Wasserfach*, **80**, 209 (1937).

¹⁴⁵ Foxwell, G. E., *Fuel*, **3**, 319 (1924). Kucherenko, N. A., *Coke and Chem. (U.S.S.R.)*, **1933**, No. 12, 63-5; *Chem. Abs.*, **29**, 8284 (1935). Jung, G., *Glückauf*, **71**, 1141-8 (1935). Spooner, C. E., and Mott, R. A., *Fuel*, **16**, 96-106 (1937). Brewer, R. E., Holmes, C. R., and Davis, J. D., *Ind. Eng. Chem.*, **32**, 930-4 (1940).

TABLE XI

CHANGES IN PROXIMATE AND ULTIMATE ANALYSIS WITH OXIDATION OF COAL: CHANGES IN PROXIMATE AND ULTIMATE ANALYSES BASED UPON THE AVERAGE FOR NINE COALS OXIDIZED AT 99.3° C (MOISTURE- AND ASH-FREE BASIS)

Oxygen consumed, percent by weight of coal	1
Days in air at 99.3° C (0 to ¼-inch coal)	4.5
Decrease in heating value, percent	0.69
Decrease in carbon content, percent of coal	0.40
Increase in oxygen content, percent of coal	0.49
Decrease in volatile matter content, percent of coal	0.6
Increase in real specific gravity of coal,* percent	0.9

* Tentative; based upon only two coals.

changes are the changes in analysis and as such are not corrected for the change in weight of coal upon oxidation. In other words, the 0.69 percent decrease in heating value is the apparent change and is larger than the true loss in heating value based upon unit weight of fresh coal.

Table XII summarizes data on losses in heating value per unit weight of coal observed in large piles of various bituminous coals. Because of the difficulty in obtaining representative samples, most of the values given are only approximate, but they show that loss in heating value does not have great commercial importance, unless serious heating should occur.

Usually the volatile-matter content of coal changes but slightly and in an irregular manner as oxidation progresses. There seems to be a tendency for minima to be reached, and the higher the original volatile-matter content the more oxidation is required to attain these minimum values.¹²⁴

Scott and Jones¹⁴⁶ oxidized anthracite

¹⁴⁶ Scott, G. S., and Jones, G. W., *U. S. Bur. Mines, Rept. Investigations*, 3504 (1940), 8 pp.

TABLE XII

PERCENTAGE LOSS IN HEATING VALUE PER UNIT WEIGHT OF COAL ON STORAGE IN LARGE PILES

Reference Number	Years of Storage	Total Percentage Loss in Heating Value	Average Annual Percentage Loss
147	2.5	3.09	1.24
17	3.0	1.66	0.55
17	0.75	0.97	1.3
16	4.5	0.50	0.11
32	10.0	1.9	0.19
9	1.25	0.91	0.73
Average	3.67	1.51	0.69

(28 to 48 mesh) for 35 days in oxygen at 300° C. Under these extreme conditions, the volatile-matter content increased from 5.7 to 57.3 percent on a pure coal basis. A weight loss of more than 78 percent of the original dry weight occurred in this period.

Scarf, Hall, and Yearsley³² found that 2½ years' outdoor storage of coal (½-inch to ⅞-inch) decreased the volatile-matter content from 37.8 to 36.5 percent, decreased the carbon content from 84.57 to 83.86 percent, increased the oxygen content from 7.62 to 8.34 percent on a dry, mineral-matter-free basis, and decreased the ash content from 11.06 to 10.03 percent.

Künle⁸¹ reported that heating a sample of bituminous coal for 10 hours at 225° C raised the oxygen content from 9.9 to 23.9 percent and increased the volatile content 1 percent. The oxygen content of fusain treated similarly increased from 5.5 to 17.4 percent. Krym⁸⁵ found that the maximum oxygen content attained on oxidation in air at 150° C corresponded to the maximum increase in weight of 9 percent and

¹⁴⁷ Olin, H. L., *Fuel*, 16, 256-8 (1937).

to the maximum hygroscopicity. This increased hygroscopicity may be due to increases in hydroxyl, carbonyl, and carboxyl groups, possibly correlating with decrease in methoxyl groups.^{122, 148}

EFFECT OF OXIDATION ON SOLUBILITY

The increase in solubility in caustic solutions is one of the most sensitive measures of the extent of oxidation of coal.^{13, 79, 90, 149} Exhaustive low-temperature oxidation of fine coal results in almost complete solubility.^{90, 150} Bunte and others⁵⁹ found that 24 hours' oxidation at room temperature increased the solubility in hot water to such an extent that it made a good measure of the extent of oxidation of the coal. The soluble material proved to be mostly oxalic acid.

Kreulen and others⁵² oxidized 125-mesh coal in oxygen at 200 to 260° C for periods up to an hour and found that the extracts in 3 to 4 percent sodium hydroxide solution (humic acid) had oxygen contents of about 28 percent. The oxygen content of the residue increased regularly with increased amount of oxidation of the coal. A second extraction with caustic solution produced about one-half as much extract as was obtained the first time. A second oxidation of the residue produced almost twice as much caustic soluble material as the first oxidation of the coal.

When coal is oxidized in alkaline solutions of chemical oxidizing agents the two processes of oxidation and dissolution occur simultaneously.¹⁵¹ The dissolved material is also attacked by the oxidizing agent.¹⁵²

With regard to solubility in organic solvents, oxidation of coal is reported to decrease the solubility to some extent for many solvents.^{123, 153} In general, both extract and residue are oxidizable in air at low temperatures,¹⁵⁴ and no very significant difference in characteristic rate of oxidation has been shown.^{90, 155} Coal extracted with pyridine showed normal behavior when oxidized in air.^{102, 156} Fischer¹²² found that a coal that showed 7.5 percent by weight of coal extractable with benzene (40 hours) and 1.5 percent with ethyl alcohol, after 30 days' oxidation at 110° C showed only 0.03 percent soluble in benzene but was soluble in alcohol to the extent of 7.4 percent. The alcohol extract of fresh coal was not soluble in ammonia, but the larger amount of extract from oxidized coal was. Oxidation of the benzene and petroleum-ether-soluble extracts (originally insoluble in ammonia) made them insoluble in these two solvents but soluble in ammonia.

RELATIVE STORABILITY OF VARIOUS COALS

Many factors other than oxidation enter into any classification of coals upon the

¹⁵¹ See Morrison, G. K., Francis, W., Gauzelin, M., and Crussard, L., in ref. 123.

¹⁵² Charpy, G., and Decors, G., *Compt. rend.*, **173**, 807 (1921). Morgan, G. T., and Jones, J. I., ref. 90.

¹⁵³ Mendelsohn, J., *J. Chem. Met. Mining Soc. S. Africa*, **33**, 285-9 (1933). Barash, M., ref. 141.

¹⁵⁴ Parr, S. W., and Hadley, H. F., *Univ. Ill. Eng. Exp. Sta., Bull.* **76** (1914), 41 pp.; *Fuel*, **4**, 31-8, 49-55, 111-8 (1925). Kuznetsov, M. I., *Khim. Tverdogo Topliva*, **6**, 515-30 (1935); *Fuel*, **16**, 114-21 (1937).

¹⁵⁵ Davis, J. D., and Reynolds, D. A., *Fuel*, **5**, 405-11 (1926).

¹⁵⁶ Schmidt, L. D., and Elder, J. L., *Ind. Eng. Chem.*, **32**, 256 (1940).

¹⁴⁸ Karavaev, N. M., Rapoport, I. B., and Kholer, V. A., *Khim. Tverdogo Topliva*, **4**, 215-35 (1933); *Chimie & industrie*, **31**, 550-1 (1934). Karavaev, N. M., Rapoport, I. B., and Kholer, V. A., *Khim. Tverdogo Topliva*, **5**, 510-25 (1934); *Chem. Abs.*, **29**, 8284 (1935). Karavaev, N. M., and Ivanov, A. K., *Mon. prod. chim.*, **18**, No. 207, 6-13 (1936); *Chem. Abs.*, **32**, 6031 (1938).

¹⁴⁹ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **1931**, 586-93. Lynch, C. S., and Collett, A. R., *Fuel*, **11**, 408-15 (1932).

¹⁵⁰ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **127**, 118-9 (1925). Fuchs, W., and Sandhoff, A. G., *Fuel*, **19**, 45-8, 69-72 (1940).

basis of how well they store. To some extent, the relative "storability" of a coal depends on the purpose for which it is destined. For example, possible impairment of coking power in storage would not be as important a factor for coals to be burned as for coals to be coked. Consequently, the relative importance of the various changes that take place in storage depends on how the coal is to be utilized.

erty of a coal. The results are expressed as the friability of the coal, that is, the percentage reduction in average particle size of lump coal caused by tumbling in a special rotating jar. The higher the friability of a coal the lower its mechanical strength and the more lumps will break up upon mechanical shock.

In Fig. 15, the friability of a number of coals is shown plotted against the percent-

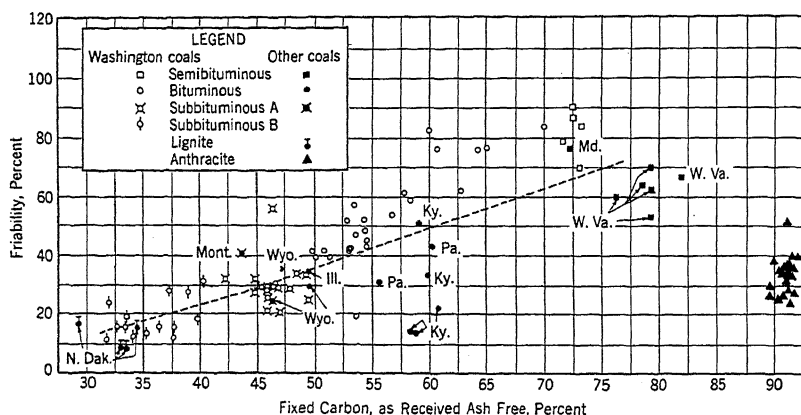


FIG. 15. The relation of the friability of American coals to fixed carbon.¹⁵⁷

The changes caused by interaction of the coal with the oxygen of the air have been discussed in some detail. They are not necessarily the most important changes from a commercial point of view. Often the amount of size degradation in handling and in storage is the factor of major importance in choice of a coal.

MECHANICAL STRENGTH OF COALS

Breakage on handling, with resultant size degradation and increase in surface exposed to air, is an important factor in the storability of a coal.

Laboratory tests¹⁵⁷ have been devised that give a practical measure of this prop-

erty of fixed carbon¹⁵⁷ on the as-received-moisture but ash-free basis. The correlation is not good, but there is a general tendency for increasing friability with increasing rank, with the notable exception of the anthracites. In other words, in general, bituminous coals of higher rank suffer higher production of fines in mining and handling, with the result that greater surface is exposed to oxidation.

SLACKING OF COAL

Exposure to the elements causes extensive degradation in the size of some coals.^{82, 84, 158, 159} This effect is particu-

¹⁵⁸ Nicolls, J. H. H., *Can. Dept. Mines, Mines Branch Rept. 671* (1927), pp. 101-5.

¹⁵⁷ Yancey, H. F., Johnson, K. A., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper 512* (1932), 94 pp.

¹⁵⁹ Fritsche, K., *Braunkohlenarch.*, No. 52, 3-44 (1939). Lavine, I., *Lignite, Occurrence and*

larly marked with subbituminous coals and lignite and is of great commercial importance for these fuels. In fact, the slacking tendency of subbituminous coal is one of the characteristics for distinguishing it from bituminous coal. This size disintegration on weathering is intimately connected with the very high natural or bed moisture content of the low-rank coals and lignite.¹⁵⁷

fuels.¹⁶¹ It consists in air-drying lumps of coal at 30 to 35 percent relative humidity¹⁶² (30 to 35° C) for 24 hours, then immersing in water for an hour and air-drying for 24 hours. The percentage of the original sample that disintegrates sufficiently to pass a 1/4-inch square screen is called the "slacking index."

In tests on a large number of coals¹⁵⁷ it

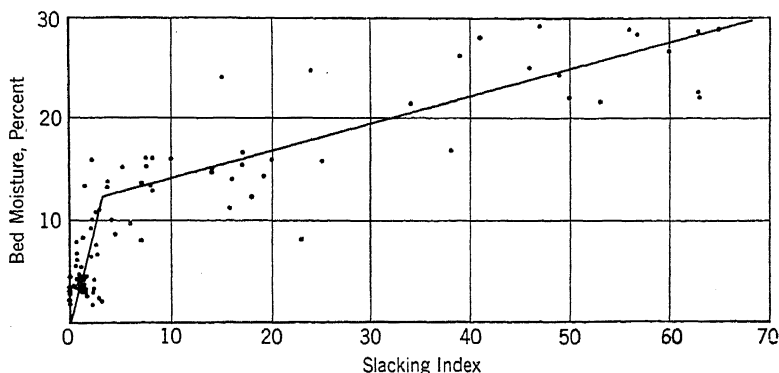


FIG. 16. The relation of the slacking index of American coals to bed moisture.¹⁵⁷

In general, coals that slack readily contain relatively large amounts of water, and loss of this moisture causes shrinkage of the coal. When the rate of moisture loss at the surface is greater than the rate of replacement by water from the interior of a piece, the shrinkage of the coal near the surface is greater than that in the interior. This unequal shrinkage causes stresses to be set up in the surface coal, with the result that the coal may crack and disintegrate. Rain on dried surfaces can also cause unequal expansion, with resultant disintegration. No slacking occurs in underwater storage.¹⁶⁰

Laboratory tests have been developed to measure the relative slacking tendency of

was found that slacking indexes ranged from nearly zero for some bituminous coals to nearly 100 for a Texas lignite. In Fig. 16 the slacking index is plotted against the bed moisture content of the coals. For coals below 10 percent bed moisture content, little trouble may be expected from slacking; above 10 percent there is a definite tendency for increased slacking.

LOSS IN COKING POWER

The rate of deterioration of coking power on storage is a very important factor in rating the relative "storability" of various coals, especially where the coal is to be stored for subsequent use in coke

Properties, Dept. of Chemical Engineering, Univ. of North Dakota, 1940, pp. 83-4.

¹⁶⁰ Nicolls, J. H. H., and Swartzman, E., *Can. Dept. Mines, Mines Branch Rept. 712* (1930), pp. 25-6.

¹⁶¹ Fieldner, A. C., Selvig, W. A., and Frederic, W. H., *U. S. Bur. Mines, Rept. Investigations 3055* (1930), 24 pp.

¹⁶² Stansfield, E., and Gilbert, K. C., *Trans. Am. Inst. Mining Met. Engrs.*, **108**, 237-42 (1934).

ovens. Extensive tests on the nine coking coals described in Table VII showed a nine-fold range in the allowable time of storage in air⁵⁸ if no serious heating occurs. That is, accelerated weathering tests indicated that coal No. 60 (a strongly coking, low-oxygen coal) could be stored in air nine times as long as coal No. 54 (a weakly coking, high-oxygen coal) before suffering serious impairment of coking power. In general, the high-volatile coals could be stored in air longer than the low-volatile coals. On the basis of a given degree of impairment of coking power, coal No. 57, a low-volatile coal, could be stored in air only one-fourth as long as coal No. 52, a high-volatile coal. This range in sensitivity of coking power to oxidation would probably be greater if a larger number of coals were tested. The loss of agglutinating power with oxidation is a good laboratory-scale measure of the sensitivity of coking power to oxidation, and data have been reported for a number of coals.^{34, 142, 163} It is to be hoped that the list of coals that have been tested in this way will be extended.

CHANGE IN COMBUSTION PROPERTIES

Aside from the small loss in heating value on storage, there are other rather poorly defined changes in the combustion characteristics of coal. The ignition temperature is raised somewhat,¹⁶⁴ and there is a decrease in the "liveliness" of the fire, accompanied by the necessity for more draft. Boiler efficiency is not necessarily decreased when stored coal is burned,¹⁰ although there may be some loss in evaporative power per unit weight of fuel.¹⁴⁷ The loss in coking power, of course, changes

the combustion characteristics, especially in the behavior on grates. In domestic underfeed stokers, the decrease in coking power resulting from storage may prove beneficial because of a decreased tendency to form coke trees.

Probably one of the major factors determining the relative storability of various coals for power-plant usage is their relative tendency for spontaneous ignition.

RELATIVE TENDENCY TOWARD SPONTANEOUS IGNITION

The characteristics of a coal that are most important in causing a tendency to ignite spontaneously are high characteristic rate of oxidation, high friability, and the presence of relatively large amounts of finely divided pyrites. Fortunately, the general increase in characteristic rate of oxidation of bituminous coals with decreasing rank of coal is at least partly compensated for by decreased friability. High characteristic rate of oxidation is often correlated with coals low in rank and with relatively high contents of bed moisture,⁴⁶ oxygen,⁶⁰ volatile matter, and pyrites.

As will be seen, the high content of moisture has some most interesting effects. In the first place, high content of natural or bed moisture is probably always associated with a large internal surface area, especially after the coal is partly dried, leaving some of the pore space available for attack by oxygen.

Most writers on the subject of spontaneous ignition list recommendations which, if followed in making storage piles, have been found by experience to lessen the chances for spontaneous ignition. No satisfactory explanation has ever been given for some of these effects; for example: (1) a rather strange but often-repeated recommendation that coals from

¹⁶³ Rose, H. J., and Sebastian, J. J. S., *Trans. Am. Inst. Mining Met. Engrs.*, 88, 556-84 (1930). Marshall, S. M., et al., ref. 141.

¹⁶⁴ Moore, B., and Sinnatt, F. S., *Fuel*, 5, 377-80 (1926).

different sources should not be piled together;²³ (2) that fresh coal should not be piled on an old pile that has weathered,¹⁴ since contact of fresh-mined coals with older seasoned coals acts as tinder at the point of contact;^{40, 165} (3) that practical men show a decided reluctance to put out fires in coal piles by means of water—as one man expressed it, “Once you begin to use water it will be necessary to keep it up as long as that lot of coal remains in storage”;¹⁶⁶ (4) that a shipment of coal that is especially wet should not be piled with other coal, and that coal should not be stored under gutters²³ where rain-water will be conducted onto the pile; and (5) that fires occur after especially rainy weather—the author has noted that practical men do not accept with good grace the explanation that previously existent fires are merely detected after rains by means of the visible evolution of steam.

It is here suggested, apparently for the first time, that this queerly assorted lot of observations and recommendations that have been without satisfactory explanation may stem from a common cause. That common cause may very well be the movement of water vapor^{12, 21, 46} through the pile, with subsequent condensation on other coal. The heat of condensation of water vapor at storage temperatures is about 580 calories per gram of water (1,040 Btu per pound). The condensation of the small amount of water required to increase the moisture content from, say, 3 percent of the weight of the coal to 4 percent is sufficient to raise the temperature of the coal more than 17° C. This rise in temperature is sufficient to increase the rate

of oxidation of the coal more than fivefold (Fig. 5). Only a small change in the relative humidity of the air in a coal pile would cause an increase of 1 per cent in moisture content of the coal and result in a great increase in the probability of spontaneous ignition. For example, where especially wet coal is piled with other coal, the sensible heat content of the wet coal would raise the temperature of drier coal in some other part of the pile and so give powerful impetus to the cycle that ends in spontaneous ignition.¹⁶⁷ Likewise, coal from different mines or fresh coal from the same mine may, by the time of arrival at the storage yard, be at equilibrium with relative humidity differing from that of the pile of coal made previously. The experience related by Hoskin,¹⁴ wherein previously dried and well-aged coal used as a base for fresh coal caused fires to appear after 13 days at the junction of moist and dry coal, could be explained as follows: the dry coal was subjected suddenly to an atmosphere at practically 100 percent relative humidity, and, in this particular case, not only the heat of condensation of water vapor would be available, but also the heat of wetting of coal,¹⁶⁸ so that the resultant temperature rise of the old, seasoned coal could be communicated by conduction and convection to points in the fresh, active coal, causing local “hot spots” to appear.

Upon the basis of the above theory, the generally unfavorable experience encountered in extinguishing hot spots or fires in coal piles by use of water could be explained by the steam formed acting as a heat-transfer agent. Heat transferred from a hot spot, usually of very limited extent,⁴⁴

¹⁶⁵ Francis, W., *Fuel*, **17**, 363-72 (1938).
Yohe, G. R., and Harman, C. A., *J. Am. Chem. Soc.*, **63**, 555-6 (1941).

¹⁶⁶ Abbott, W. L., *Factory*, **26**, 969 (1921).
Hoskin, A. J., *Purdue Univ. Exp. Sta., Bull.* **30**, (1928), p. 45.

¹⁶⁷ It can be shown that, if coal at equilibrium with a relative humidity of 50 percent is covered with wet coal at the same temperature, a rise of 11° C in the drier coal may result.

¹⁶⁸ Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper* **113** (1916), 80 pp.

where the compensating effect of low oxygen concentration is, no doubt, already holding the fire in check, to a large volume of the pile where oxygen is still available in ample quantities could easily aggravate matters instead of helping, unless large enough quantities of water are available to cool essentially the whole pile. Rainy weather could cause new fires to appear by this same process. Of course, when hot spots or fires can be flooded quickly enough so that no appreciable quantities of steam are formed, no difficulties arise. For example, forcing pipes into a pile and then flooding with water and a limestone slurry under pressure proved successful in extinguishing a spoil-bank fire.¹⁶⁹ As coal does not wet readily, the use of chemical wetting agents in the water should prove practicable.

SUMMARY AND CONCLUSIONS

Changes that occur in coal on storage depend on the following occurrences: (1) all the visible constituents, except ash and moisture, of all coals consume oxygen from the air; and (2) moisture loss from high-moisture subbituminous coals and lignite causes slacking or size degradation.

The rate of the oxidation reaction (1) increases by a factor of 2.2 for each 10° C rise in temperature, (2) increases with the 0.61 power of the oxygen concentration in the air, (3) apparently increases proportionally to about the cube root of the specific surface area of the coal, and (4) decreases with time or extent of oxidation in accordance with a simple quantitative relationship wherein the rate of decrease depends on the particle size of the coal.

The characteristic rate of oxidation—a of coal—is usually high for coals

of (1) high natural or bed moisture content, (2) high oxygen content, (3) high volatile-matter content, and (4) high content of finely divided pyrites. In general, the characteristic rate of oxidation is low for high-rank coals.

Spontaneous ignition occurs when conditions are such that the rate of heat evolution from the oxidation reaction continuously exceeds the rate of heat dissipation from the coal pile. Its occurrence is favored by high characteristic rate of oxidation, but the conditions of storage usually are more important. More data are needed on the effective oxygen concentrations in large coal piles and the effect of different methods of storing on this factor. The action of water vapor as a heat-transfer agent in coal piles should be studied.

Barring serious spontaneous heating, the loss in heating value that occurs on storage usually is not large enough to have great commercial importance. The loss in coking power has great commercial importance, especially in coals to be used in coke ovens. The best measures of loss in coking power upon oxidation include: (1) actual carbonization on a scale large enough so that the properties of the coke can be investigated, (2) change in agglutinating value, and (3) changes in plastic properties, such as expansion pressure. More sensitive methods of measuring the extent of oxidation of coal are needed. At present the best measures include the increased solubility in caustic solution and the decrease in heating value.

As a suggestion, new methods could take advantage of the large decreases in rate of oxidation and in yield of tar with increased extent of oxidation or of the increased oxygen content of coal by means of more precise methods for the direct determination of oxygen in coal.

¹⁶⁹ Price, H., *Colliery Guardian*, 154, 533-5 (1937).

THE ACTION OF SOLVENTS ON COAL

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Of the many methods of studying the thermal decomposition of coal, solvent action, because of its mild pyrolyzing effect, is one of greatest interest. The more drastic a treatment in an investigation becomes, the more inferential become the conclusions permissible from the data. Rigorous oxidation indicates the presence of benzenoid, pyrrol, and furane rings in the parent substance and in the lower-rank coals such as peat, brown coal, and lignite; milder oxidation shows a great part of the coal mass to be humic in nature. Distillation of coal is carried out at temperatures so high that there is a possibility of molecular rearrangements. Ultimate and proximate analyses may tell something with respect to age, rank, behavior on carbonization, and industrial significance, but nothing with regard to structure or constitution. To determine accurately the nature of coal, experimental procedures, milder in nature than the above, have been sought. To many investigators solvent action has appeared of value. Unlike the more drastic treatments, extraction leaves the greater part of its products similar to the original coal except in molecular size.

An indication of the interest displayed for this phase of coal research can be obtained from the large number of papers which have been published embodying the results obtained from extraction of coal

from almost every deposit of significance. In spite of the amount of experimental data available, lack of standardization in procedures and materials has increased the difficulty with which one investigator's work may be related to another's.

The soluble products of extraction, whether they are called extracts or bitumens, vary according to the mechanism by which they are obtained. Thus, certain constituents such as oils, fats, acids, alcohols, esters, resins, hydrocarbons, and waxes occur in various coals as occluded or loosely bound materials. On the other hand, a part of the extract appears to have originated as a result of the thermal depolymerization of the coal and another part from the solvent depolymerization. In addition to producing materials which seem to be in true solution, some solvents, notably pyridine, bring about a process of peptization or colloidal dispersion of the coal substance. An extract might, therefore, contain quite a mixture of organic substances ranging from more or less familiar low-molecular-weight compounds to highly complex molecules and colloids.

Solvent analysis has been applied to coal for a number of reasons. Attempts have been made to explain various coal properties, coking behavior, rank, degree of oxidation, and so forth, on the basis of the action of a number of solvents. Chemists

have tried to attack the problem of chemical constitution of coal indirectly through a study of extraction products. With a few notable exceptions, it has been possible to identify only those compounds which occur as occluded materials. In addition, the literature contains reports on studies of the various variables of extraction such as time, temperature, coal-particle size, vapor heating, and the effect of the chemical and physical nature of the solvent.

The word bitumen, already referred to, has been somewhat loosely employed by many coal chemists. In one sense, it is used to designate those materials which, upon heating, produce a significant amount of volatile substances like gas or tar, or which melt, swell, or coke when heated. Fischer and Gluud¹ designated as bitumen all constituents of coal which, upon dry distillation, produced tar, water, and gas. On the other hand, in extraction studies, bitumens are generally considered to be the soluble materials of coal. The term has been subdivided according to the method by which the soluble substances are obtained. Several workers have recom-

mended that those materials rendered soluble by boiling benzene at a pressure of 1 atmosphere be called "bitumen A" and occasionally the ethanol-benzene (1:1) soluble part of coal is so designated. However, soon after the introduction of the use of solvents as a tool in studying coal constitution it was found that extractions carried out under pressure produced a greater yield of extract in a much shorter period of time. Since this additional material which is dissolved by the increased temperature, the cause of the increased pressure, differs from that obtained at ordinary pressures, a need was felt for a differentiation between extracts obtained by these two methods. Schneider and Tropsch² recommended that the incremental yield brought about by pressure extraction be called "bitumen B." Extracts with compositions covering a wide range should be obtained at different pressures depending on the temperature, any of which could be considered bitumen B. Occasionally a "bitumen C"³ has been referred to as the material made soluble in benzene or ethanol-benzene, when the bitu-

² Schneider, W., and Tropsch, H., *ibid.*, **2**, 57-64 (1917).

³ Stadnikoff, G., *Die Chemie der Kohlen*, Ferdinand Enke, Stuttgart, 1931, p. 105.

¹ Fischer, F., and Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 1-38 (1918).

TABLE I

YIELDS OF BITUMENS FROM VARIOUS COALS

	Tschermichowsches Seam ⁴					Chachareiskys Boghead Coal ⁴				Sphagnum Peat ⁵	Boldyrewsky Seam Upper Stratum Kuznets	Coal Kuznets Basin ⁵
	Brown Coal Stratum	Brown Coal Stratum	Brown Coal Stratum	Bituminous Coal Stratum	Bituminous Coal Stratum	Stratified	Compact	Stratified				
	1	5	7	10	13							
Bitumen A, per cent		6.1	8.2	8.4	8.1	3.5	8.3	5.7	3.7	18.2	0.43	0.62
Bitumen B, percent	Trace	Trace	Trace	...	0.8	1.0		2.5	2.1		2.47	3.8
Bitumen C, percent	6.5	3.1	1.8	1.6	1.5	2.7	2.4	0.7	4.4	5.5	1.65	7.8

⁴ Stadnikoff, G., *Die Entstehung von Kohle und Erdöl*, Ferdinand Enke, Stuttgart, 1930. Chap. VI.

⁵ Stadnikoff, G., *Neuere Torfchemie*, Theodor Steinkopff, Leipzig, 1930, p. 117.

men-A-free coal is boiled with 10 percent hydrochloric acid. The origin of this additional soluble material has been attributed to the effect of the acid on the inorganic salts of acids in the coal.⁶ A general idea of the magnitude of these fractions can be obtained from Table I.

THE EXTRACTION OF PEAT

The relationship between yield and the age of a coal is far from definite; moreover, great inconsistencies exist in coals of the same apparent ages. Explanation of these facts hardly belongs in this section; however, a few pertinent general statements might partly explain the origin of these variations. The yield of extract, mainly waxes and resins, from plants and wood, obtained under identical conditions, has been shown^{7, 8} to be dependent on the type of plant or wood. If these waxes and resins are carried over in the peat formation in a generally unchanged form, then a partial explanation of the variation of yield with different peats may be obtained merely by postulating different origins for the peat. It is true that no direct relationship may exist, but the great difference in the content of soluble material of various woods (a few tenths to 15 or 20 percent) should make this a factor. Certain mechanical factors may also exist, such as segregation and distribution of the resins and waxes by differences in density.

⁶ Schwalbe, C. G., *Brennstoff-Chem.*, **3**, 80 (1922).

⁷ Wiegmann, A. F., *Über die Entstehung, Bildung, und das Wesen des Torfes*, F. Vieweg u. Sohn, Braunschweig, 1837. Hoering, P., *Moor-nutzung und Torfverwertung*, Julius Springer, Berlin, 1915, pp. 193-5. Fischer, F., and Kleinstück, M., *Ges. Abhandl. Kenntnis Kohle*, **3**, 301-14 (1918). Kurth, E. F., *Ind. Eng. Chem., Anal. Ed.*, **11**, 203-5 (1939).

⁸ Strache, H., and Lant, R., *Kohlenchemie*, Akademische Verlagsgesellschaft m.b.H., Leipzig, 1924, p. 175.

Early in the study of the action of solvents on coals it was found that certain mixtures of solvents were capable of yielding larger amounts of bitumens than could be obtained with the individual components. This is not a new concept limited to the solution of coal. It may be recalled that certain cellulose nitrates are soluble in a mixture of ether and alcohol although they are insoluble in either solvent alone. Reilly, et al.⁹ have made a remarkably thorough study of yield and properties of bitumens (called wax) obtainable from Irish peat with numerous single solvents, azeotropic mixtures, and two-phase systems of solvents. In addition, a considerable amount of distillation data which should be of industrial significance were included. The peat studied was dried for 1 hour at 100° C and then extracted in Soxhlets to exhaustion (about 16 hours). Comparison of the yields obtained with solvent mixtures, given in Tables II and III, and the yields with single pure solvents, given in Table IV, shows that greater yields are obtained with the solvent mixtures than with the pure components alone. Some of the waxes were extracted on a large scale. The products were hard and black, and the authors felt that they had commercial possibilities both as waxes and as sources of fatty acids of high molecular weight.

The constants of the waxes were determined by the usual analytical procedures. The melting points were determined by the open-capillary-tube method. The "ether solubility" figure was thought to be an index of the "resin" content of the waxes and was obtained by washing a 0.5-gram sample of the powdered wax with successive 10-cubic-centimeter portions of cold ethyl ether until the ether was no longer colored.

⁹ Reilly, J., Kelly, D. E., and Ryan, D. J., *J. Soc. Chem. Ind.*, **56**, 231-8T (1937).

TABLE II

YIELD OF PEAT EXTRACT OBTAINED WITH AZEOTROPIC MIXTURES ⁹

Solvent Mixture and Percentage Weight Composition	Boiling Point of 1st Com- ponent °C	Boiling Point of 2nd Com- ponent °C	Boiling Point of Azeotropic Mixture °C	Yield of Wax from Anhydrous Peat percent	Saponi- fication Value of Wax	Acid No.	Ester Value	Iodine Value	Ether Solu- bility	White Spirit Solu- bility	Melt- ing Point °C
Benzene (67.6)											
Ethanol (32.4)	80.5	78.5	68.5	14.3	193	61	132	16	44	89	74
Benzene (83.0)											
n-Propanol (17.0)	80.5	98	77.1	15.8	133	47	86	16	52	95	72
Benzene (63.5)											
Terbutanol (36.5)	80.5	82.8	73.9	12.3	144	58	86	20	55	96	73
Benzene (66.7)											
Isopropanol (33.3)	80.5	82.3	71.9	15.6	127	66	61	14	49	80	78
Benzene (90.7)											
Isobutanol (9.3)	80.5	107.4	79.9	10.7	146	51	95	33	52.5	99.5	72
Benzene (80)											
Allyl alcohol (20)	80.5	97	76.7	14.2	175	78	97	18	45.2	99	75
Benzene (98)											
Acetic acid (2)	80.5	117.8	80.1	13.3	156	69	87	16	49	99.5	74
Ethyl acetate (69)											
Ethanol (31)	77.2	78.5	71	17.7	197	84	113	33	51.9	88	76
Acetic acid (27)		138.8									
m-Xylene (73)	117.8	139.2	114	18.1	161	52	109	18	52	80	77
Ethanol (6)											
Chloroform (94)	78.5	61.2	59.3	14.6	200	72	128	35	51.6	93	74
Methanol (10)											
Chloroform (90)	64.5	61.2	53.5	16.7	200	72	128	25	55	75	70
Acetone (80)											
Chloroform (20)	56.1	61.2	64.7	15.0	145	66	79	18.3	63.2	75	73
Ethanol (16)											
Carbon tetrachloride (84)	78.5	76.8	64.9	15.4	148	50	98	25	57.7	99	76
Carbon tetrachloride (57)											
Ethyl acetate (43)	76.8	77.2	74.7	9.7	158	64	94	16	53	96-97	75
Toluene (70)											
Acetic acid (30)	110.7	117.8	104	15-17	179	61	118	19	42.5	85	75
Acetone (86)											
Methanol (14)	56.1	64.5	55.9	14.2	173	63	110	24	57	80	70
Acetone (55)											
Methyl acetate (45)	56.1	57.1	56.1	15.6	196	79	117	23	55	80	70
Carbon tetrachloride (79.4)											
Methanol (20.6)	76.8	64.5	55.7	11.0	151	63	88	24	51	83	71
Hexane (98.8)											
Isobutanol (1.2)	69.0	107.4	69.1	6.1	67	33	34	28	58	100	69
Carbon disulfide (90.7)											
Ethyl alcohol (9.3)	46.3	78.5	42.4	7.3	128	63	65	24	53	99-100	71
n-Propanol (28.3)											
Toluene (71.7)	98	110.7	87.7	18	58	39	119	23	51.6	80	72
Ethanol (89.5)											
Toluene (10.5)	78.5	110.7	76.6	12.4	170	45	115	25	50	92	73

TABLE III

YIELD OF PEAT EXTRACT OBTAINED WITH TWO-PHASE SOLVENT SYSTEMS^a

Solvent Mixture and Percentage Weight Composition	Yield percent	Saponi- fication Value	Acid Value	Ester Value	Iodine Value	Ether Solubility	White Spirit Solubility	Melting Point °C
Trichloroethylene (80) Ethanol (14) Water (6)	15.8	154	67	87	16	42	70	72.5
Trichloroethylene (67) <i>n</i> -Propanol (27) Water (6)	12.6	159	54	105	23	46	69	74
<i>n</i> -Propanol (9) Benzene (82) Water (9)	14.1	140	53	87	19	46	83	73
Benzene (74.1) Ethanol (18.5) Water (7.4)	15.1	175	63	112	22	51	71	72.5
Carbon tetrachloride (84) <i>n</i> -Propanol (8.5) Water (7.5)	14.1	180	62	118	16	59	80	72
Carbon tetrachloride (82) Ethanol (12) Water (6)	14.8	176	65	111	21	59	70	71.5
Cyclohexane (84) <i>n</i> -Propanol (12) Water (4)	10.6	121	63	58	21	35	99-100	69.5
Chloroform (85) Methanol (10) Water (5)	13.3	174	46	128	22	33	74	70
Chloroform (92) Ethanol (4) Water (4)	12.9	193	63	120	23	33	83	72
Benzene (93) Acetic acid (1.2) Water (5.8)	9.1	156	51	105	24	37	99-100	69

The amount soluble was then determined by evaporating the ether. The "white spirit solubility" was determined in an analogous fashion except that the washing was carried out with the hot solvent.

The authors called attention to the fact that the average yield in Table V was about 7 percent, which would approximately represent the amount of petroleum-soluble material in the peat. On the other hand, the benzene-*n*-propanol mixture, for example, gave a yield of 15 percent, of which 95 per-

cent was soluble in white spirit. This represents a petroleum-soluble wax content of 14.2 percent in the peat. The difference, they explained, was due to a surface-tension effect; the petroleum was not "wetting" the peat. Perhaps another explanation might lie in a depolymerization mechanism in which the large molecules, after being broken down by the first solvent, were soluble in the second poorer solvent. The extent to which such a depolymerization might go would be a function, first, within

TABLE IV
 EXTRACTION OF PEAT WITH PURE SOLVENTS ⁹

Solvent	Yield percent	Saponi- fication Value	Acid Value	Ester Value	Iodine Value	Ether Solu- bility	White Spirit Solu- bility	Melt- ing Point °C
Methanol	9.2	195	105	90	29	49	80	70
Ethanol	14.0	178	59	119	28	54	75	74
<i>n</i> -Propanol	18.6	180	83	97	25	51	85	74
Isopropanol	15.5	231	92	139	25	53	80	71
<i>n</i> -Butanol	17.4	173	72	101	29	53	75	73
Isobutanol	9.3	214	83	131	29	70	75	73
Pentanol	16.7	188	71	117	28	54	83	73
<i>sec</i> -Hexanol	13.3	190	60	130	22	44	80	74
Benzene	9	71	39	32	31	49	100	69
Toluene	10.9	150	63	87	31	55	100	69
<i>m</i> -Xylene	11.1	170	65	105	29	55	100	70
Mesitylene	11.8	157	50	107	21	55	100	68
Hexane	5.2	85	40	45	24	46	100	69
Cyclohexane	6.8	121	60	61	25	50	100	69
Methyl acetate	13.6	210	90	120	31	55	80	69
Ethyl acetate	13.7	204	85	119	30	57	85	70
<i>n</i> -Propyl acetate	11.0	214	80	134	31	44	92	70
<i>n</i> -Butyl acetate	9.4	200	73	127	30	50	99	69
Acetone	11.4	149	73	76	24	50	88	70
Chloroform	9.7	132	56	76	22	53	99.5	72
Carbon tetrachloride	8.8	114	50	64	24	40	100	75

 TABLE V
 EXTRACTION OF PEAT WITH PETROLEUM FRACTIONS ⁹

Fraction Distillation Range	Yield percent	Saponi- fication Value	Acid Value	Ester Value	Iodine Value	Ether Solu- bility	White Spirit Solu- bility	Melt- ing Point °C
70-89	7.5	101	47	54	25	38	100	70
70-140	7.1	113	68	45	24	49	100	70
77-95	8-10	66	33	33	30	45	100	70
100-120	6.0	96	48	48	29	48	100	71
Above 150 (White spirit)	9.7	118	60	58	27	53	100	69

limits, of temperature, and second, of the physical nature of the solvent.

Fischer and Schneider,¹⁰ in studying the extraction of cellulose (*Kahlbaum*) with solvents, reported yields which were near the lower limit of the values obtained for peat. In these studies it was found that a 6-hour Soxhlet extraction of cellulose (5.04 percent moisture content) with benzene at the boiling point gave an average yield of 0.34 percent on the basis of the dry cellulose. Pressure extractions carried out in a bomb with benzene at 250 to 260° C gave yields of 2.0 percent with cellulose dried at 105° C, 6.4 percent with air-dried cellulose, and 12 percent when the extraction was carried out in the presence of water. The effect of water during the extraction was probably one of hydrolysis. The method of drying was important. Relative to this, Schneider and Schellenberg¹¹ have shown that in the benzene extraction of air-dried peat more material is dissolved than when the peat is dried at 105° C. It was found that if water was added to the dried material the yield was not increased as it was with brown coal. It was the opinion of Strache and Lant¹² that a temperature of 105° C is too low to favor the formation of insoluble material through a polymerization mechanism, but, as they pointed out, fusible substances in the peat which are insoluble in benzene may melt at this low temperature and cover, or admix with, the benzene-soluble constituents.

It was shown by Rau¹³ that extractions carried out with benzene under a pressure of 14 atmospheres yielded much greater amounts of soluble material. Fischer and

Gluud,¹⁴ working with still higher pressures, 50 to 55 atmospheres, were instrumental in opening up an entirely new field of possibilities in the extraction of coal.

Schneider and Schellenberg,¹¹ using the method of Fischer and Gluud, carried out a number of extractions on peats at several temperatures with benzene and alcohol, together with atmospheric Soxhlet extractions with the same solvents. The benzene extract obtained in a Soxhlet was yellow brown, more or less transparent, brittle, waxlike, softening at 50° C and melting at 70 to 72° C. The acid number of the investigated extracts ranged from 34.5 to 73.3. The saponification number for the bitumen of Lauchhammer peat amounted to 202.5. (For comparison: the acid number of montan wax is about 35, and its saponification number is in the neighborhood of 80.) The material was only partly soluble in hot alcohol and was precipitated upon cooling. The ether-soluble products had a resinlike character; the ether-insoluble portion consisted of a gray-brown powder melting at 81° C. The extract from the alcohol extraction of peat at atmospheric pressure showed, in general, a higher melting point than the benzene extract.

It was found that samples taken at different layers of a peat bog gave extracts which were soluble in benzene and alkali in a definite ratio, depending on the source of the peat. Thus, alcohol extracts from samples 1, 2, and 3 of Velen peat, though differing slightly in appearance and their melting points, were approximately 40 percent soluble in benzene and 60 percent soluble in alkali regardless of the depth from which the samples were taken in the bog. The value of the ratio of benzene to alkali

¹⁰ Fischer, F., and Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 287-300 (1918).

¹¹ Schneider, W., and Schellenberg, A., *ibid.*, **5**, 1-33 (1920).

¹² See p. 177 of ref. 8.

¹³ Rau, O., *Stahl u. Eisen*, **30**, 1235-46, 1282-97 (1910).

¹⁴ Fischer, F., and Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, **1**, 54-63 (1915-6); *Ber.*, **49**, 1460-8 (1916).

solubility was found to vary from one peat to another. The extract obtained at 250° C with alcohol was more resinlike than that obtained with benzene. With both solvents the bitumens were soft, sticky, and dark brown and had a pitchlike odor. Their melting points were under 100° C. The authors¹¹ pointed out that the extracts obtained at atmospheric pressure with benzene resembled the corresponding products from brown coal and were oil-free, whereas the extracts obtained at 150° C contained oils, which must have resulted from a degradation process. The amount of oil was found to increase with increasing temperature. It was further found that as the temperature was increased beyond 200° C no increase in yield took place, remaining about the same up to 250° C, while the amount of residue decreased, indicating the formation of water and volatile products.

The extraction of Velen peat with phenol at the boiling point by these same authors¹⁵ yielded a product (36.3 percent) with properties quite different from the above. The extract, dark in color, had a higher melting point than the benzene pressure extract from the same peat. The extract was found to be incompletely soluble in benzene even at 250° C.

Schneider and Schellenberg also carried out extractions of peat with characteristic cellulose solvents¹⁵ and with water.¹⁶ The data from the first investigation are given in Table VI. It was concluded from this work that the cellulose reagents had no essential dissolving capacity for peat since the yields, based on the insoluble residue, were only a little lower in general than with alkali alone. The data from the second paper are summarized in Table VII.

¹⁵ Schneider, W., and Schellenberg, A., *Ges. Abhandl. Kenntnis Kohle*, 5, 34-6 (1920).

¹⁶ Schneider, W., and Schellenberg, A., *ibid.*, 5, 372-6 (1920). See also Reinsch, H., *J. prakt. n.*, 22, 188-91 (1880).

TABLE VI

EXTRACTION OF PEAT WITH COLD CELLULOSE SOLVENTS¹⁵

	Percent Insoluble after Treatment with			
	NaOH Alone	Xanthogenic Acid	NH ₃ Alone	Schweitzer Reagent
Velen Sample 1	85	83	94	70
Velen Sample 2	74	69	88	83

TABLE VII

EXTRACTION OF PEAT (VELEN) WITH WATER¹⁶

Temperature °C	Time of Extraction hours	Residue percent	Extract percent	Extract + Residue percent
250		67.5		73.8
250		62.9	13.7	76.6

The products of these extractions had peculiar properties. They were insoluble in benzene and only partly soluble in alcohol and water. Partial solubility in aqueous sodium hydroxide and sodium carbonate indicated the presence of acidic material. As in other extractions, the material balances at 250° C were less than 100 percent, indicating the production of water, carbon dioxide, volatile acids, and aldehydes.

Several investigators have been successful in identifying a few organic compounds found in peat extracts. These substances have been, in general, those which would be found in living plants or which might have been derived from plant material through such simple changes as hydrolysis or decarboxylation. However, these studies have been limited to a relatively small part of the extract, and little is known of the chemical nature of the remaining part except that it contains groups or structures which are easily polymerized by moderate heating.

Working with peat from a Wisconsin bed 3 meters, or 10 feet, in thickness, Thiessen and Johnson¹⁷ brought about a separation

¹⁷ Thiessen, R., and Johnson, R. C., *Ind. Eng. Chem., Anal. Ed.*, 1, 216-20 (1929).

into water-soluble, alcohol-soluble, alkali-soluble, humic acids, lignin, cellulose, insoluble constituents, and mineral matter. The cold-water-soluble matter ranged from 1 to 3 percent, increasing from the top to the bottom of the bed. The hot-water-soluble material was 4.25 percent near the surface and fairly constant below the first 0.3 meter (12 inches) at 3.5 to 4.0 percent. The total water-soluble material ranged from 5 to approximately 7 percent, increasing in general from the top to the bottom of the bed. This fraction contained reducing sugars, pentosans, methyl pentosans, nitrogenous compounds, and some humic material. The ether-soluble material fluctuated between 2 and 6.6 percent and contained chiefly fats, waxes, resins, and some chlorophyll. The lignin content was highest near the surface, 36 to 44 percent, and decreased to approximately 10 percent at the bottom. The relative amount of alkali-soluble material was lowest near the surface and increased to 51 percent at the bottom. The cellulosic material was, on the other hand, highest near the surface, about 40 percent, and decreased to mere traces at the bottom. The insoluble material tended to increase slightly from top to bottom, ranging from 4 to 23 percent. Similar results were obtained from other parts of the deposit and from different deposits.

A second paper¹⁸ by these authors treated the nature of the alcohol-soluble and parts of the ether-soluble fractions more extensively. The peat after drying at 105°C was crushed to pass a 15-mesh screen and subsequently leached with 1 percent hydrochloric acid to remove about 75 percent of the mineral matter. The amount of alcohol-soluble material was increased 25 to 50 percent by this acid treat-

ment. Between 2 and 6 percent of this acid-treated peat was soluble with ether in a Soxhlet. The extract was a light brown or yellow waxlike substance. On treatment of the ether extract with 10 percent solution of sodium bicarbonate, a dark brown aqueous solution separated which yielded a precipitate when treated with hydrochloric acid. This was not investigated further. The remaining ether solution contained a wax which had a melting point, saponification number, acid number, and iodine value similar to montan wax. Chlorophyll was also isolated from the ether solution. The alcohol-benzene extract from the bottom several feet of the bog, which contained the largest amount of chlorophyll, yielded a small quantity of xanthophyll and carotin. The presence of chlorophyll in peat had been reported as early as 1880 by Guignet,¹⁹ who also reported the identification of glucosides, and in 1907 by Zalosiecki and Hausmann.²⁰

The dried ether extract was extracted with alcohol in a Soxhlet and then treated according to the scheme shown on page 686. The raw alcohol extract constituted, in part, the hymatomelanic acid of Odén.²¹ The general properties of several of the various fractions were described.

Fraction 1, about 0.5 percent of original extract, was a sweet-smelling brown, oily substance soluble in water, acids, bases, and ether. It was not investigated.

Fraction 2 was sweet-smelling, dark brown to black, viscous, soluble in water and alcohol, and insoluble in ether. It formed a dark red solution in water. It reduced Fehling's solution and also an am-

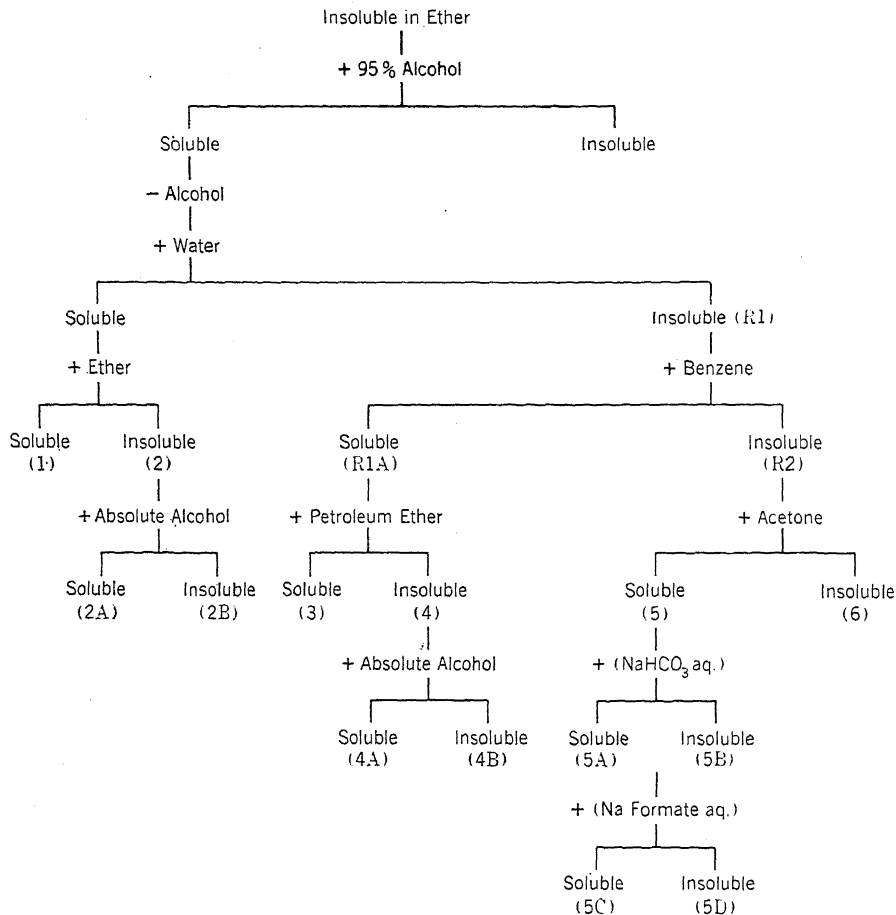
¹⁹ Guignet, C. E., *Compt. rend.*, **91**, 888-9 (1880).

²⁰ Zalosiecki, R., and Hausmann, J., *Z. angew. Chem.*, **20**, 1141-3 (1907).

²¹ Odén, S., and Lindberg, S., *Brennstoff-Chem.*, **7**, 165-70 (1926).

¹⁸ Johnson, R. C., and Thiessen, R., *Fuel*, **13**, 44-7 (1934).

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moniacal silver nitrate solution, gave the Molisch test for carbohydrates, and formed osazones.

Fraction 2A was a brown, viscous material which formed a dark red solution in water that became yellow on treatment with animal charcoal. Osazones prepared from fractions 2A and 2B, after being purified, melted at 149 and 159° C. Fraction 2B was somewhat similar to 2A. Arabinose was thought to be present since the formation of the osazone prepared resembled the formation from the known compound. The

melting point was 159 against 160° C for the osazone of arabinose.

Fraction 3A was a yellow, viscous oil which, upon standing, yielded yellowish bisphenoidal crystals which were identified as sulfur. The remaining yellow oil was not investigated.

It was not possible to identify any constituents of the other fractions, although the chemical groups into which they fell could be established on the basis of their solubilities. By Kamm's scheme of analysis, fraction 4 would be grouped with the

alcohols, acids, aldehydes, ketones, quinones, acetates, esters, and lactone anhydrides. Phenolic and acidic materials were found in fractions 5B and 5C.

Although the authors stated that the above separation was not complete, it did indicate the fact that the initial extract was capable of separation into a considerable number of substances. The results show the complexity of peat of which the fractions here considered were but a small part.

Extractions carried out by Stadnikoff and Titov²² on Russian peat with samples taken at different depths in the bog showed the same fluctuation in yield reported by other workers. There was, however, a tendency for the yield to increase with depth. It was further shown in the same paper that the bitumens could be separated into crystalline, waxlike, and amorphous substances by extracting with an alcohol-ether mixture. Successive extractions with benzine and benzene served to bring about a separation of the wax and resins. The bitumens were about 45 percent wax and 55 percent resin. In investigating a concept introduced in an earlier publication,²³ namely, that bitumens could be polymerized by moderate heating, it was found that, after the extract from sphagnum peat was heated for 12 hours at 140° C, 11.9 percent was insoluble after successive extraction with benzine, chloroform, and carbon disulfide. When the temperature was raised to 180° for another 12 hours, the insoluble residue increased to 29.0 percent. The same treatment applied to bitumens from carex peat gave 1.4 percent insoluble after the 140° heating and 27.7 percent after heating at 180° C. The

paper would indicate that the bitumens which were given this heat treatment were obtained with alcohol-benzene, so that one might assume, since there are no statements to the contrary, that all this material might not be soluble in the successive extractions with benzine, chloroform, and carbon disulfide; hence the figure given for percent residue after the 140° heating loses significance. However, the increase in insoluble residue which took place by further heating at 180° well proves the argument in favor of polymerization. This is an important point, and it will be found that polymerization of parts of the coal substance is not limited to peat alone. Heating the peat before extraction²⁴ has been shown to bring about the same decrease in solubility. As Stadnikoff and Titov pointed out, the formation of peat involves the production not only of relatively simple saturated and unsaturated compounds but also of high-molecular-weight polymerization products. The same paper gave data on the comparative destructive distillation of extract, residue, and peat which indicated that, in the initial stages of distillation, polymerization of the resins is involved.

Titov,²⁵ working with the sphagnum peat studied in the preceding paper, was able to isolate several apparently pure compounds from the benzine-soluble portion. After fractionation of the original extract with ether and alkali, he obtained, from 800 grams of an unsaponifiable part of the benzene-soluble material, 164 grams of an almost colorless substance which had a melting point of 75 to 76° C. The empirical formula was $C_{35}H_{72}$, and the observed molecular weight was 499.0 (calculated for $C_{35}H_{72}$, 492.9). This hydrocar-

²² Stadnikoff, G., and Titov, N. G., *Brennstoff-Chem.*, **9**, 357-8 (1928); *Zhur. Priklad. Khim.*, **1**, 328-30 (1928).

²³ Stadnikoff, G., Mehl, P., and Putzilo, W., *Brennstoff-Chem.*, **6**, 338-6 (1925).

²⁴ Kondrat'ev, E. V., and Kutniev, S. K., *Khim. Tverdogo Topliva*, **6**, 403-8 (1935); *Chem. Abs.*, **29**, 7614 (1935).

²⁵ Titov, N. G., *Brennstoff-Chem.*, **13**, 266-9 (1932).

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bon appeared to be pentatriacontane (m.p., 74 to 75° C). From further fractionation of the ether-soluble material 80 grams of a colorless substance with the formula $C_{33}H_{68}$ and melting point of 70.5 to 71.5° C was isolated corresponding to tritriacontane (m.p., 71.8° C). The calculated molecular weight was 464.8 against the observed value of 461.9. Another substance, melting at 74 to 75° C and having the formula $C_{27}H_{56}O$, was also obtained (18 grams). This was apparently an alcohol (acetyl number 136.7 against 127.9 calculated for $C_{27}H_{56}O$). The alcohol did not add halogen and appeared to be a saturated aliphatic compound. The same ether-soluble fraction contained material having hydroxyl groups (acetyl number 11.8–12.0). Through further treatment a mixture of alcohols of vaseline-like consistency was isolated (9.3 grams). The acetyl number was 125, the iodine value 33.3, and the average composition C 78.95 percent, H 12.11 percent. From the saponifiable part of the original extract, Titov separated, by fractionation of the ethyl esters, four acids, $C_{12}H_{22}O_2$, $C_{14}H_{26}O_2$, $C_{25}H_{50}O_2$, and $C_{27}H_{54}O_2$, which appeared to be pure compounds. The above procedure was repeated, using the benzene-soluble part of the peat as a starting material. The products isolated in this fashion were identical to the above except that an unknown compound, $C_{30}H_{60}O_3$, was thought to have been isolated. The author concluded that the bitumens from peat were quite different from those obtained from brown coal and that the resinous part of the extract contained esters of cyclic acids and saturated and unsaturated alcohols.

In another study of Russian peat, by Rakovskii and Edelstein,²⁶ the bitumens ob-

tained by ethanol-benzene extraction were further subdivided by using methanol (0.5 percent acetone) to remove 33 percent resinous material. Further treatment of the resin-free bitumens with alcohol and benzene yielded 13 percent wax of which 57 percent was crude fatty acids. From this fraction it was possible to separate acids having the formulas $C_{26}H_{52}O_2$, $C_{27}H_{54}O_2$, and $C_{28}H_{56}O_2$. In this paper attention was called to the ability of the bitumens to polymerize easily and oxidize when they were heated on a water bath.

Zalosiecki and Hausmann²⁰ were able to isolate an acid with a melting point of 184° and an alcohol, $C_{26}H_{40}O_4$, melting at 124 to 130° C by extracting the peat first with alcohol and then further separating the extract with ether and by saponification. Additional separation yielded an acid, $C_{21}H_{35}O_7$, which did not melt at temperatures as high as 260° C.

From soil humus and peat soils which might be considered related to peat, Schreiner and Shorey²⁷ isolated α -hydroxystearic acid, $C_{18}H_{36}O_3$; paraffinic acid, $C_{24}H_{48}O_2$; lignoceric acid, $C_{24}H_{48}O_2$, and dihydroxystearic acid, $C_{18}H_{36}O_4$. In the first paper these authors gave a synthesis which might easily take place in nature and which indicates the possible origin of complex material found in coal. When pyruvic acid reacts with ammonia, uvitonic acid is produced. This compound, upon heating to 274° C, gives picoline carboxylic acid, which was found in soil humus. Pyruvic acid is known to result from the decomposition of protein material, or it can be produced in other ways, such as oxidation of glycols or heating tartaric acid, any one of which could take place in nature. A temperature of 274° C may appear high, but

²⁶ Rakovskii, E. V., and Edelstein, N. G., *Brennstoff-Chem.*, **13**, 46–9 (1932).

²⁷ Schreiner, O., and Shorey, E. C., *J. Am. Chem. Soc.*, **30**, 1295–307, 1599–607 (1908), **32**, 1674–80 (1910).

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it is only at this temperature that the rate of reaction reaches a measurable value. Lower temperatures would cause the reaction to proceed at a slower speed. Picoline carboxylic acid is a cyclic nitrogen-containing acid. In addition, the above authors were able to isolate a sulfur-containing compound, trithiobenzaldehyde. Only rarely have definite sulfur or nitrogen compounds been reported as isolated from peat or from the higher coals.

Aschan²⁸ has reported the isolation of an acid, $C_{19}H_{34}O_2$, from Finnish peat. The melting point of this compound was 72 to 73° C. The isolation of two acids, $C_{16}H_{25}O_5$ and $C_{21}H_{35}O_7$, and a substance having the formula $C_{20}H_{40}O_4$, has been reported by Zalosiecki and Hausmann.²⁰ The benzene extract of a Russian peat studied by Roginskaya²⁹ had a softening temperature of 70 to 73°, saponification number 158, acid number 49.7, and iodine number 27.9. The alcohol extraction of this extract gave 53 percent of wax with a softening temperature of 76° C. Saponification of this wax gave a 40 percent yield of potassium soaps. The acids which were obtained were purified by crystallization and fractionation of their methyl esters. Three acids, $C_{29}H_{58}O_2$, $C_{28}H_{56}O_2$, and

$C_{27}H_{54}O_2$, were isolated. The presence of an acid of lower molecular weight and the absence of hydroxy acids were indicated.

Bone and coworkers, whose work will be taken up in some detail later, have divided the extract into a number of general fractions according to the scheme shown below. Fraction I was subdivided into Ia (volatile with steam) and Ib (not volatile). It was found by Bone and Tei³⁰ that earthy brown coals and peat yielded fractions I and II, but not III and IV, their place being taken by III' and IV', which were neutral phenolic esters and acid phenolic bodies, respectively.

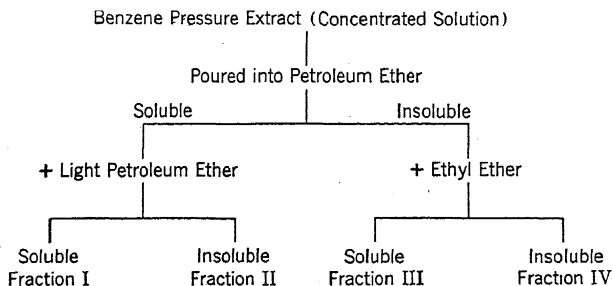
When the above scheme was applied to the benzene extract obtained from the pressure extraction (210, 260, and 285° C) of well-rotted Tarraun Irish peat, the following fractions were obtained from the dewaxed peat: I(a), 3.6 percent; I(b), 2.5 percent; II, 1.7 percent; III' and IV', 4.4 percent. The extract also contained tarry material. Some water and carbon dioxide were split out of the peat on heating. The results were thought to indicate that the origin of fractions III and IV obtained in the extractions of bituminous coals lies in the phenolic compounds comprising fractions III' and IV' of peat and brown coals.

The change of solubility of various peat samples with the depth in the bed has al-

²⁸ Aschan, O., *Brennstoff-Chem.*, **2**, 316 (1921); *Torfwirtsch.*, **2**, 9 (1921).

²⁹ Roginskaya, E. V., *J. Applied Chem. (U.S.S.R.)*, **9**, 108-11 (1936); *Chem. Abs.*, **30**, 5441 (1936).

³⁰ Bone, W. A., and Tei, L. J., *Proc. Roy. Soc. (London)*, **A147**, 58-67 (1934).



ready been mentioned. In some beds³¹ the yield seemed to increase in proportion to the depth; in others, only a slight or no tendency to do so is found.^{16, 17, 21, 32} Many natural forces such as segregations according to density and mixing by moving water were probably responsible to a large extent for these inconsistencies.

THE EXTRACTION OF BROWN COAL

The foregoing and some additional data^{33, 34} indicate that the yield of extract obtainable from peat with a given organic solvent varies over a considerable range, the amount obtained depending not only on the age of the peat but upon the origin and method of deposition as well. It is found that these same fluctuations in yield exist in the higher-rank coals, at least in part as a natural consequence of their early history. In general, however, it is found that for solvents such as benzene a maximum is reached on the yield of extract *versus* rank curve near the region of the young brown coals.²¹ In going through the series:

plant → peat → brown coal, a number of changes such as destruction of cellulose and the transformation of lignin to humic acids take place, resulting in a relative increase in the amount of the more stable waxes and resins. Accompanying this change there is an increase in the thermal stability of the products of extraction. This increase in stability is not toward polymerization by heat but rather toward loss of water and gas upon moderate heating (200 to 250° C). Bone, Horton, and Tei³⁵ reported that in the extraction of several brown coals with benzene in a high-pressure Soxhlet only a young brown coal underwent a loss of even a small amount of gas and water and this at 250 to 280° C. Fischer and Schneider³⁶ reported that brown-coal extractions carried out at temperatures from 155 to 260° C were accompanied by loss of gas. However, the loss was not indicated to be anywhere near that which would have been obtained with peat under identical conditions.

In general, the bitumens of brown coal are distributed evenly through the coal mass. Exceptions, however, are occasionally encountered. Some brown-coal deposits contain layers of bituminous coals.^{37, 38} A New Zealand brown coal (Central Otago), examined by James,³⁹ was found to be non-homogeneous with respect to its resin content. The resin, disseminated throughout the mass of the coal, ranged from very small, barely visible pieces to more or less spherical lumps of all sizes up to 20 centimeters in diameter. Certain sections of the coal were especially rich in

³¹ Stadnikoff, G., *Kolloidchem. Beihefte*, **31**, 56-88 (1930). Waksman, S. A., *Brennstoff-Chem.*, **11**, 277-81 (1930).

³² Stadnikoff, G., and Baryschewa, A., *Brennstoff-Chem.*, **11**, 21-3 (1930).

³³ Doppler, C., *Sitzber. Akad. Wiss. Wien Math. naturw. Klasse*, **3**, 239-40 (1849). de Molon, *Compt. rend.*, **92**, 139-42 (1881). Frank, F., *Mitt. Ver. Förderung Moorkulture*, **20**, 228 (1902). Holde, D., *Mitt. Materialprüfungsamt Berlin-Lichterfelde West*, **27**, 23-24 (1909). See p. 101 of ref. 3. Hoering, P., pp. 235-40 of ref. 7. Tidswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **121**, 2345-62 (1922). Marcusson, J., *Z. angew. Chem.*, **40**, 48-50 (1927). Stadnikoff, G., and Titov, N. G., *Brennstoff-Chem.*, **9**, 325-6 (1928). Tokmanov, G., *Gornyi Zhur.*, **106**, 107-15 (1930). Waksman, S. A., and Stevens, K., *Ind. Eng. Chem., Anal. Ed.*, **2**, 167-73 (1930). Aschan, O., *Tek. Fören. Finland Förrh.*, **54**, 285-88 (1934); *Chem. Abs.*, **29**, 1230 (1935). Sihvonen, V., and Lundmark, E., *Suomen Kemistilehti*, **10A**, 130-5 (1937). Stefanovski, W., and Dominik, Z., *Przegląd. Chem.*, **1**, 73-7 (1937).

³⁴ Krämer, G., and Spilker, A., *Ber.*, **32**, 2940-59 (1899); **35**, 1212-23 (1902).

³⁵ Bone, W. A., Horton, L., and Tei, L. J., *Proc. Roy. Soc. (London)*, **A120**, 523-45 (1928).

³⁶ Fischer, F., and Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **1**, 204-10 (1915-6).

³⁷ See pp. 165 and 167 of ref. 4.

³⁸ Fuchs, W., *Die Chemie der Kohle*, Julius Springer, Berlin, 1931, p. 171.

³⁹ James, L. H., *J. Soc. Chem. Ind.*, **44**, 241-2T (1925).

resin, concentrated in bands which could be followed for great distances. Many of the lumps showed a concentric shell structure. The resin had an acid value of 44.3, saponification value 46.2, iodine value 174.4, and a maximum solubility in chloroform. The melting point of the soluble part of the resin ranged from 60 to 120° C, depending on the solvent used. Data were presented indicating that the resin was similar to Kauri resin. It might be pointed out that the resins extracted from peat, brown coals, lignite, and the higher coals, like other fossil resins, differ generally from the resins extracted from living plants in being less fusible and less readily soluble in organic solvents. The bituminous-coal resins are richer in carbon and considerably poorer in hydrogen than peat, brown-coal, and lignite resins.⁴⁰

The soluble products obtained from the atmospheric-pressure extraction of brown coal with low-boiling solvents such as alcohol, benzene, toluene, like those obtained from peat, are largely waxes and resins. The separation and purification of these two general groups of compounds have been dealt with at some length in the literature and many high-molecular-weight compounds have been isolated from both groups. These easily extractable materials are of significant importance both as a source of industrial materials and as a means for studying the coalification process.

Montan wax, so named by von Boyen,⁴¹ obtained by the large-scale extraction of

coal,⁴² has been of some industrial significance for a number of years. It has found use at one time or another in the production of such items as shoe polish, phonograph rolls, insulating materials, candles, and polishes, and it has special applications in the rubber industry. In addition, its use as a binder in the fabrication of coal briquets has been proposed. The possibility of using the resins of coal in varnish has also been discussed in the literature.⁴³

The yield⁴⁴ and, to some extent, the properties of montan wax depend on the source of the coal and the solvent. The data in Table VIII were obtained by Stein-

TABLE VIII

YIELDS AND PROPERTIES OF BROWN-COAL EXTRACTS⁴⁵

Coal	Yield of Extract percent	Acid Number	Saponification Number	Ester Number
Fürstenberg	23.7	28.6	97.8	69.2
Phönix	9.4	34.4	157.8	123.4
Werminghoff	8.0	34.5	154.6	120.1
Kassel	9.2	68.6	262.1	193.6
Fortuna	6.3	31.8	130.9	99.1
Corona	33.9	30.4	134.4	104.1
Hirschfelde	36.6	9.4	119.7	110.3

brecher⁴⁵ from the extraction of a number of brown coals with ethanol-benzene (1:3). Extraction of the resulting residue with pyridine resulted in the further solution of about 6 to 7 percent based on the original coal. By fractionation of the bitumen from these coals with benzene and acetone, a separation was made between resin-free benzene-soluble wax, acetone-in-

⁴⁰ Wigginton, R., *Fuel*, **5**, 476-8 (1926); **7**, 118 (1928). See also White, D., and Thiessen, R., *U. S. Bur. Mines, Bull.* **38** (1913), 390 pp. Engler, C., and Tausz, J., *Z. angew. Chem.*, **34**, 308-9 (1921). Wheeler, R. V., and Wigginton, R., *Fuel*, **1**, 12-4 (1922). Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **129**, 1410-2 (1926).

⁴¹ Von Boyen, E., *Z. angew. Chem.*, **12**, 64-5 (1899), **14**, 1110-1 (1901).

⁴² Baerlocher, G. O., *Farben-Chem.*, **9**, 191-3, 198 (1938); Ullmann, F., *Enzyklopädie der technischen Chemie*, **2**, 616-20 (1928), Urban & Schwarzenberg, Berlin, 1928.

⁴³ Benson, H. K., *Ind. Eng. Chem.*, **17**, 21-3 (1925).

⁴⁴ Donath, E., *Brennstoff-Chem.*, **1**, 86-7 (1920).

⁴⁵ Steinbrecher, H., *Braunkohlenarchiv*, No. **12**, 40-91 (1926); *Brennstoff-Chem.*, **10**, 198-201 (1929).

soluble wax, and an acetone-soluble wax-free resin. The amounts and chemical properties of these fractions are shown in Table IX. The saponification number of

TABLE IX

COMPOSITION OF WAXES AND RESINS IN THE EXTRACTS OBTAINED FROM BROWN COALS ⁴⁵

Coal	Wax		Acetone Wax		Resin	
	Yield	Acid	Yield	Acid	Yield	Acid
		Number		Number		Number
	percent		percent		percent	
Fürstenberg	74.7	32.9	9.4	12.5	15.9	10.0
Phönix	62.0	35.1	8.6	36.0	29.4	24.5
Werminghoff	59.7	27.6	10.0	14.5	30.3	20.9
Kassel	55.3	7.6	19.9	37.1	25.7
Fortuna	54.8	24.7	15.1	16.8	30.1	20.9
Corona	39.3	44.5	6.0	26.9	54.7	14.4
Hirschfelde	13.2	22.9	7.2	17.5	79.6	6.5

the product obtained with alcohol-benzene was higher than that obtained with alcohol alone. The montan wax obtained with benzene had a higher melting point than that obtained with benzine. Both these properties indicate a higher molecular weight for the wax.

In general, montan wax has the following properties: ⁴⁶ acid number, 20 to 30; saponification number, 60 to 80; iodine number, 12 to 19; specific gravity, near 1; heat of combustion, 9,700 calories per gram; and flash point, 300° C. A sample of montan wax (resin-free) obtained by Schneider ⁴⁷ from a brown coal (Riebeck Montanwerke) had a melting point of 80° C; acid number, 23; saponification number, 95; methoxyl number, 2.0; and heat of combustion, 9,896 calories per gram. The elementary analysis for the sample was: carbon, 79.6 percent; hydrogen, 12.7 percent; sulfur, 0.8 percent; and ash, 0.6 percent. These properties, with the exception

of the saponification number, fall within the limits indicated above.

Krämer and Spilker ⁴⁸ were among the first to observe that the crude montan wax contained resinlike materials. Graefe ⁴⁸ has shown that a separation of the wax and resins can be brought about by dissolving the crude material in hot alcohol which then precipitates the wax upon cooling, leaving the resins in solution. A more quantitative separation can be achieved by fractionating with ether in which the wax is insoluble. Fischer and Gluud ⁴⁹ have found that liquid sulfur dioxide is an effective solvent for separating the wax and resins, and there is evidence ⁵⁰ that an acetone-sulfur dioxide (1 : 1) mixture will also fractionate this mixture. Pschorr and Pfaff ⁵¹ extracted bitumens with ether and acetone and obtained a sticky, ether-soluble resin fraction. Some further subdivision of the bitumens is occasionally encountered. Steinbrecher ⁴⁵ separated the extract into benzene-soluble and -insoluble waxes, acetone-insoluble waxes, and benzene- and acetone-soluble resins.

The resin content of brown-coal bitumens is far from constant. For example, Graefe ⁴⁸ found that montan wax from pyropissite contained only 6.64 percent resin; bitumens from Riebeck brown coal, 16.54; bitumen of the firm of Heimann, 46.66; montan wax from Bohemian coal, 31.54; and Silesian montan wax, 65.90.

⁴⁸ Graefe, E., *Braunkohle*, **3**, 242 (1904); *Braunkohlen- u. Brikkettind.*, **29**, 297 (1921), **30**, 59 (1922); *Brennstoff-Chem.*, **3**, 56-7, 59-60 (1922). See also Schneider, W., and Jantsch, O., *Ges. Abhandl. Kenntnis Kohle*, **4**, 363-72 (1919).

⁴⁹ Fischer, F., and Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, **1**, 64-7 (1915-6); *Ber.*, **49**, 1469-74 (1916).

⁵⁰ Schmitt, G., *Petroleum Times*, **8**, 249-50 (1922).

⁵¹ Pschorr, R., and Pfaff, J. K., *Ber.*, **53**, 2147-62 (1920); *Z. angew. Chem.*, **34**, 334-6 (1921).

⁴⁶ Graefe, E., *Laboratoriumsbuch für Braunkohlenteerindustrie*, W. Knapp, Halle, 1908, p. 152.

⁴⁷ Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 325-57 (1919).

Patzschke⁵² found that the bitumen from Oberlausitzer brown coal contained 80 to 82 percent resin and only 18 to 20 percent wax. Schneider⁴⁷ reported that a brown coal from the Riebeck Montanwerke yielded 15 percent montan wax, of which 2 percent was resin and 13 percent wax. A Bohemian brown coal, the entire extract of which was composed of resin, has been reported.⁵³

Schneider⁵⁴ reported the following properties and analysis of montan resin: melting point, 65 to 70°C; acid number, 33; saponification number, 76; methoxyl number, 3.4; carbon, 78.4 percent; hydrogen, 10.5 percent; sulfur, 1.3 percent; ash, 0.9 percent; and heat of combustion, 9,255 calories per gram. The resin from Oberlausitzer brown coal studied by Patzschke,⁵² which contained 18 percent wax, had the following properties: softening point, 68.0°C; drop point, 97.5°C; and saponification number, 119. Patzschke was able, through further refining of the crude resin, to obtain a high-melting resin which was completely saponifiable (saponification number, 260). It resembled colophonium and formed insoluble aluminum salts which could serve for sizing paper. The dielectric constant of this material was higher than that of rubber and ebonite. The properties of montan resin given by Marcusson and Smelkus⁵⁵ are: acid number, 42.9; saponification number, 73.2; iodine number, 22.9; and specific gravity, above 1.

Graefe⁴⁸ treated a large quantity of Weibau montan wax with 90 percent ethanol and obtained a residue, alcohol-soluble resins, and alcohol-insoluble waxes which had

the physical and chemical properties given in Table X.

Chemical investigation of the resins of brown coal has indicated again the complexity of the soluble material of coal and has shown to some extent the method of formation and origin of the highly condensed systems found in the higher-rank coals. The work of Marcusson and Smelkus,⁵⁵ as well as that of Steinbrecher,⁵⁶ has

TABLE X

PROPERTIES OF CONSTITUENTS OF WEBAU
MONTAN WAX⁴⁸

Property	Resin	Wax	Residue
Specific gravity (15° C)	1.063	1.008	1.013
Melting point, °C	72	76	82
Acid number	27.5	49.5	28
Ester number	28	61.6	30
Saponification number	55.5	111.1	58
Distillation gave:			
Distillate, percent	67	74.0	66.0
Coke, percent	10.4	8.0	9.2
Gas, percent	22.6	18.0	24.8
Distillate was:	Liquid, dark brown	Solid, but- terlike, yellowish	Solid, but- terlike, yellowish
Specific gravity of distillate	0.981	0.994
Acid number of distillate	19.3	20.0	16.0
Ester number of distillate	28.0	33.6	28.0
Saponification number of distillate	47.3	53.6	44.0

indicated the terpene nature of the resins obtained from brown-coal bitumens. Soltys⁵⁷ isolated a hydrogenated polyterpene, C₂₀H₃₄, iosenene, in small quantities from Styrian brown coal. Iosenene is a retene derivative, identical with hartite. Soltys thought that it was probably likewise identical with bombicite and hofannite, reported earlier,⁵⁸ and with the hydrocarbon

⁵⁶ Steinbrecher, H., *Brennstoff-Chem.*, **12**, 163-5 (1931). See also: Jurasky, K. A., *Brennstoff-Chem.*, **12**, 161-3 (1931).

⁵⁷ Soltys, A., *Monatsh.*, **53/54**, 175-84, 185-6 (1929).

⁵⁸ Ciusa, R., and Galizzi, A., *Gazz. chim. ital.*, **51**, I, 55-60 (1921). Ciusa, R., and Croce, M., *ibid.*, **52**, I, 125-8 (1922).

⁵² Patzschke, F. W., *Brennstoff-Chem.*, **2**, 59-60 (1921).

⁵³ See p. 182 of ref. 8.

⁵⁴ Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **5**, 46-8 (1920).

⁵⁵ Marcusson, J., and Smelkus, H., *Chem.-Ztg.*, **41**, 129-32, 150-1 (1917).

isolated from brown coal by Dolch and Strebinger.⁵⁹ The petroleum-ether-soluble fraction of the original extract contained a saturated tricyclic sesquiterpene with the formula $C_{15}H_{26}$, which was characterized only by analysis. From 1 kilogram of the same coal, Soltys was able to isolate from 0.1 to 0.3 gram of an optically active compound ($[\alpha]_D^{25} = -19.1$ in benzene) which melted at $256^\circ C$ and had the formula $C_{30}H_{50}O$. This compound apparently had a sterollike structure. Another optically active hydrocarbon, $C_{15}H_{28}$, ($[\alpha]_D^{25} = +5.62$), which melted at $265^\circ C$ was also found. Walden⁶⁰ as early as 1906 had detected a dextrorotatory substance in coal bitumen.

From the extraordinarily complicated mixture found in a brown-coal resin, Ruhemann and Raud⁶¹ were able to isolate a small quantity of crystalline sterols and terpene derivatives. A middle German brown coal was treated in an extractor which worked on the Soxhlet principle with ethanol-benzene, and the bitumens obtained were separated into wax and resin fractions with ether,⁴⁸ in which the wax is insoluble, and then a further separation was carried out by precipitating the remaining wax from a benzene solution of the ether-soluble part with acetone at temperatures below $0^\circ C$.⁴⁵ The resulting crude resin had the following analysis and chemical constants: C, 76.4 percent; H, 10.3 percent; O + S + N, 13.3 percent; saponification number, 93.1; acid number, 14.6, and ester number, 78.5. The neutral unsaponifiable resin material, in addition to small amounts of high-molecular-weight paraffin alcohols isolated by Pschorr and

Pfaff⁶² also contained a colorless crystalline substance melting at $346^\circ C$. Analysis gave a formula for the compound, $C_{30}H_{48}O_3$, isomeric with hydroxyallobetulinol. Upon attempted acetylation it was found to contain no hydroxyl, nor did the oxygen appear to be carbonyl since no reaction took place with phenylhydrazine. Hence, it was concluded that all three oxygens were in ether linkages or heterocyclic configurations, and it was pointed out that the compound might have originated in a sterol in which the hydroxyl groups of allobetulinols had undergone isomerization to form a cyclic compound—a commonly encountered reaction in sterol chemistry. The compound differed from most sterols in being completely saturated. The terpene nature of the material was indicated by reduction with hydriodic acid in a sealed tube at 200 to $250^\circ C$ to yield a polyterpene (C_5H_8)_n.

In another series of experiments by these same authors; brown coal was extracted with ethanol-benzene to give an 8.8 percent yield of bitumens of which 11.8 percent was soluble in petroleum ether (60 to $70^\circ C$ fraction) and 21.8 percent was soluble in methyl alcohol. Two paraffin hydrocarbons, triacontane, $C_{30}H_{64}$, melting at 64 to $65^\circ C$, and dotriacontane, $C_{32}H_{64}$, melting at 70 to $71^\circ C$, were isolated from the petroleum ether fraction. The petroleum ether extract was also found to contain polyterpenes. The methanol-soluble extract was found to contain the isomer of hydroxyallobetulinol referred to earlier and an unidentified primary alcohol, $C_{20}H_{40}O_2$ (melting point, $250^\circ C$). It also contained a small amount of 4-isopropylidenecyclohexanone. It is of interest to note that this last compound results from the isomerization of nopinone with dilute acids and that nopinone is a product of the oxidation of β -pinene. The saponifiable portion of this extract was found to contain betulinol,

⁵⁹ Dolch, M., and Strebinger, R., *Mikrochemie*, **2**, 94–8 (1924).

⁶⁰ Walden, P., *Chem.-Ztg.*, **30**, 1155–8, 1167–70 (1906).

⁶¹ Ruhemann, S., and Raud, H., *Brennstoff-Chem.*, **13**, 341–5 (1932). Pschorr, R., and Pfaff, J. K., *Ber.*, **53**, 2147–61 (1920).

$C_{30}H_{50}O_2$, melting point 254 to 255° C, allobetulinol, $C_{30}H_{50}O_2$, melting point 264 to 265° C, hydroxyallobetulinol, $C_{30}H_{48}O_3$, melting point 336 to 337° C, and its isomer.

The saponification of montan wax (resin-freed material) is much more difficult than saponification of the resin. Whereas the reaction of the resin takes place easily with aqueous alkali, alcoholic potassium hydroxide must be used for the wax. Fischer and Schneider⁶² found that at 200° C under pressure montan wax could be saponified with sodium carbonate solution. Tropsch and Kreutzer,⁶³ Diltthey,⁶⁴ and Koch⁶⁵ saponified the wax with 5 N aqueous potassium hydroxide in an autoclave at 160 to 170° C. Concentrated hydrochloric acid at 110 to 120° C will not cleave the wax esters. The unsaponifiable part of the wax can be dissolved away from fatty acid salts with acetone.

Krämer and Spilker⁶⁴ isolated an alcohol with 20 to 22 carbon atoms from the unsaponifiable part of the wax. Hübner⁶⁶ indicated the probable presence of ketones, $C_{16}H_{32}O$ and $C_{12}H_{24}O$, in the same fraction and the presence of a solid paraffin (melting point 52–53°) which was probably decosane. Ciusa and Galizzi⁶⁷ separated the crystalline compounds, $C_{15}H_{20}$, "simonellite," $C_{15}H_{28}$, $C_{15}H_{26}$, and $C_{22}H_{34}$ from the ether extract of the unsaponifiable portion of a Fognano brown coal.

The action of chloronitric acid on montan wax yields chloro and nitro com-

pounds.⁴¹ Montan wax is susceptible of oxidation with potassium permanganate and dichromate in acid or basic solution, and it is possible, through choice of conditions, to obtain light yellow to pure white products by such means. Treatment with fuming or concentrated sulfuric acid brings about the formation of a char from which an almost white wax can be extracted in small amounts with solvents such as benzene.

It has already been pointed out that the long heating of peat bitumens at moderately high temperature results in their partial conversion to benzene-insoluble substances. The same process takes place with brown-coal extracts⁶⁸ in which the carbon and hydrogen contents are decreased by about 1.5 percent.

Montan wax is also oxidizable in air at higher temperatures in somewhat the same manner as paraffins. Oxidation with air takes place rapidly at higher temperatures under pressure in the presence of alkali.⁶⁹ Fischer and Schneider⁷⁰ have studied the effect of a stream of air on montan wax at 200° in the presence of aqueous sodium carbonate. From this treatment there resulted an almost clear solution of sodium salts having poor lathering properties. Longer treatment resulted in the formation of soaps of fatty acids ($C_{12}H_{24}O_2$ to $C_{18}H_{36}O_2$). Montan wax which has been heated to 340 to 350° C shows an increased resistance to pressure oxidation. Distilled montan wax is slightly oxidizable under pressure. Fractional crystallization of the sodium salts of the fatty acids from the wax will take place at room temperatures to give soluble soaps with good lather-

⁶² Fischer, F., and Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **4**, 180–209 (1919).

⁶³ Tropsch, H., and Kreutzer, A., *Brennstoff-Chem.*, **3**, 49, 177–80, 193–8, 212–5 (1922).

⁶⁴ Tropsch, H., and Diltthey, P., *ibid.*, **6**, 65–9 (1925).

⁶⁵ Koch, H., *ibid.*, **10**, 82–6 (1929). Tropsch, H., *ibid.*, **10**, 403–4 (1929).

⁶⁶ Hübner, C., dissertation, Halle, 1903, p. 20; *Arch. Pharm.*, **244**, 196–215 (1906).

⁶⁷ Ciusa, R., and Galizzi, A., *Ann. chim. applicata*, **15**, 209–14 (1925); *Zentralbl.*, **97**, I, 278 (1926).

⁶⁸ Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **4**, 48–93 (1919).

⁶⁹ Fischer, F., *ibid.*, **4**, 13–25 (1919).

⁷⁰ Fischer, F., and Schneider, W., *ibid.*, **4**, 48–93 (1919). Fischer, F., *ibid.*, **4**, (1919).

forming properties. The yield of fatty acids from the pressure oxidation of montan wax, according to Strache and Lant, is lower than from paraffin since the higher fatty acids are attacked only after those of average molecular weight have been destroyed.

The oxidation of montan wax with ozone has also been studied. Fischer and Tropsch⁷¹ treated 10 grams of the wax with 6 percent ozone and found that the dark-colored solution changed to light yellow after only a half an hour of treatment. After 24 hours, the total weight of the reaction products was 12 grams. The resinous material was separated from the wax by boiling the mixture with benzine (boiling point, 100 to 120°) in which the resin was insoluble. The waxlike product had an average equivalent weight of 368. Fractionation of this material with alcohol gave an equivalent weight of 520 for the least soluble part and 288 for the soluble fraction. A similar treatment, when applied to so-called montanic acid, yielded fragments of about half the molecular weight of the original acid. Fischer and Schneider,⁷² in a later paper, showed that, whereas low-temperature tar paraffins and montan wax are easily oxidized with ozone to water-insoluble acids at 50 to 60° C, hard paraffins and preheated montan wax are much more resistant to this treatment.

The distillation of montan wax has been investigated by a number of workers. Von Boyen⁴¹ obtained a tallowlike material melting at 55 to 60° C from the distillation of the wax. Krämer and Spilker³⁴ obtained semi-liquid paraffin hydrocarbons. To avoid the apparent drastic decomposition they also carried out distillations un-

der reduced pressure and obtained a yellowish, waxlike material melting at 74 to 78° C. The distillation of montan wax by Graefe has already been referred to.

From the unsaponifiable fraction obtained from distillation of montan wax, Eisenreich⁷³ obtained a substance containing 2.57 percent oxygen, which Grün and Ulbrich⁷⁴ believed to be a ketone formed from montanic acid. This compound they named montanone.⁷⁵ The melting point of the distilled wax was lower than that of the raw material, the iodine number was higher, and the molecular weight lower. Moreover, the acid content of the distilled product was lower than the original. The distillation was accompanied by a loss of water, carbon dioxide, carbon monoxide, and hydrogen sulfide, and by the formation of pitch. Ketones such as those found in the distillate could have had their origin in the loss of carbon dioxide and water from two molecules of acid.

The distillation of montan wax with superheated steam (250° C) and subsequent treatment of the resulting material with decolorizing agents, according to von Boyen,⁷⁶ produced a white crystalline prod-

⁷³ Eisenreich, K., *Chem. Rev. Fett- u. Harz-Ind.*, **16**, 211-3 (1909); *Chem. Zentr.*, **80**, II, 1088 (1909).

⁷⁴ Grün, A., and Ulbrich, E., *ibid.*, **23**, 57-60 (1916). See also ref. 55.

⁷⁵ There is a considerable amount of confusion in the literature concerning the formula of montanic acid. Grün and Ulbrich used $C_{23}H_{50}O_2$, as did Fischer and Tropsch (see ref. 71). Others, Strache and Lant and Fuchs, used $C_{20}H_{38}O_2$. The ketone referred to above according to Grün and Ulbrich was $(C_{27}H_{54})_2C=O$.

⁷⁶ Von Boyen, E., *Ger. Pat.* 101,373 (1897). For other purification methods see: Nathanson, F., *Ger. Pat.* 220,050 (1906). Wachs- u. Ceresin-Werke, *Ger. Pats.* 237,012 (1908), 254,701 (1908), 247,357 (1909). Iena, E., *Ger. Pats.* 411,541 (1922), 411,542 (1922). A. Riebeck'sche Montanwerke, *Ger. Pats.* 447,530 (1923), 449,297 (1925), 556,150 (1927), 556,407 (1929). Schlickum-Werke A.-G., *Ger. Pat.* 491,161 (1924). I. G. Farbenindustrie A.-G., *Ger. Pats.* 451,187 (1926), 553,296 (1926), 462,373

⁷¹ Fischer, F., and Tropsch, H., *ibid.*, **2**, 169-72 (1917).

⁷² Fischer, F., and Schneider, W., *ibid.*, **5**, 117-28 (1920).

uct which melted at 70 to 80° C. The properties given by Marcusson and Smelkus⁵⁵ for steam-distilled wax were: acid number, 42 to 123; saponification number, 62 to 127; iodine number, 9.8 to 12.0; ether number, 1.5 to 10.7; melting point, 73 to 80° C; montanic acid content, 32.0 to 93.2 percent; unsaponifiables, 6.8 to 68.0 percent.

Montan wax has been subjected to a considerable number of investigations, the chief purpose of which has been the isolation and identification of its various chemical constituents. Some of these, which occur in the resin part of the wax and distillate, have already been indicated. Many more have been found in the wax itself. As early as 1852, Brückner⁷⁷ had isolated an acid from Gerstewitz brown coal. This compound, which melted at 82° C, he called "geocerinic acid." The analysis of the lead salt indicated the formula to be $C_{28}H_{56}O_2$. This compound had been obtained by the superheated-steam distillation of montan wax (refined wax) in which some decomposition might have taken place. Hell,⁷⁸ who made a further study of this compound, obtained the free acid by saponifying refined montan wax with alkali, extracting the soaps with ligroin, and decomposing the acid salts with mineral acid. The resulting acids melted at 83 to 84° C. This was followed by a systematic fractionation by precipitation of the acids with magnesium acetate. The melting points of the acids from the various fractions were close together, and it was found that the value could not be increased beyond 84.5° C. Elementary analysis of the free acid gave a formula $C_{26}H_{52}O_2$. Hell converted one of the fractions to the methyl ester and

fractionated this at 14 millimeters. It was found to distil over at 296 to 298° C. The melting point of this fraction was just under 84° C, and the analysis of the lead salt fitted best the formula $C_{26}H_{52}O_2$. Hell came to the conclusion that the acid part of the brown-coal bitumens was composed almost entirely of this acid and that it differed completely from the acids generally found in waxes. These workers based their formulas on the analysis of the lead salts, which are of such molecular size that the difference between C_{28} and C_{29} would be close to the experimental error so that a formula thus established is hardly unquestionable. A more accurate method would be the determination of the equivalent weight by titration of the acid with alcoholic alkali. The difference in equivalent or molecular weight between a C_{28} and a C_{29} acid is 14, a value well outside the experimental error. Eisenreich⁷⁹ has confirmed the formula of Hell and reported a melting point of 82.5° C.

Later research, however, indicated that the formula $C_{29}H_{58}O_2$ was in error, and $C_{28}H_{56}O_2$ was reported as being correct. Ryan and Dillon⁷⁹ obtained a yellowish white wax from Irish peat that, upon recrystallization from alcohol, yielded montanic acid which melted at 83° C and to which they ascribed the formula $C_{28}H_{56}O_2$. Easterfield and Taylor⁸⁰ obtained an acid from montan wax that, upon repeated crystallizations from alcohol and glacial acetic acid, melted at 82.5° C. The titration value agreed with the formula $C_{28}H_{56}O_2$. On the basis of a thorough investigation, Meyer and Brod⁸¹ obtained a titration value of

(1927). Johnson, J. Y., Brit. Pat. 305,552 (1929). Weiler, *Chem.-Ztg.*, **62**, 761-3 (1938).

⁷⁷ Brückner, L., *J. prakt. Chem.*, (1), **57**, 1-21 (1852).

⁷⁸ Hell, C., *Z. angew. Chem.*, **13**, 556-7 (1900).

⁷⁹ Ryan, H., and Dillon, T., *Sci. Proc. Roy. Dublin Soc.*, **12**, 202-9 (1909); *Chem. Zentr.*, **84**, II, 2048-9 (1913).

⁸⁰ Easterfield, T. H., and Taylor, C. M., *J. Chem. Soc.*, **99**, 2298-307 (1911).

⁸¹ Meyer, H., and Brod, L., *Monatsh.*, **34**, 1143-57 (1913).

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426.2 against 424.4 calculated for (which certainly seems a justification of the C_{28} formula. Their system of fractionation and purification was quite long and elaborate. The work of Pschorr and Pfaff⁵¹ indicated the C_{28} acid to be correct on the basis of an equivalent weight of 426. At the same time these authors isolated several higher alcohols from the saponified montan wax. Acetylation of the nonacid fraction with acetic anhydride and subsequent fractional crystallization of the resulting product yielded tetracosanol, $C_{24}H_{50}O$ ⁵² (melting point 83° C), ceryl alcohol, $C_{26}H_{54}O$ (melting point 79° C), and myricyl alcohol, $C_{30}H_{62}O$ (melting point 88° C). An unidentified crystalline compound, $C_{24}H_{34}O_2$, was also isolated.

Kliegl, Schmid, and Merkel⁵³ attempted to solve the montanic acid problem by synthetic methods by studying the relationship between montanic, cerotic, and melissic acids. The montanic acid was converted to the amide and this by the following steps to montyl chloride: $R \cdot CONH_2 \rightarrow R \cdot CN \rightarrow RCH_2NH_2 \rightarrow R \cdot CH_2 \cdot NHCOC_6H_5 \rightarrow RCH_2Cl$. This last compound was allowed to react with sodium malonic acid ester, yielding $RCH_2CH_2 \cdot COOH$, which was identical to melissic acid, $C_{31}H_{62}O_2$. The inference, therefore, was that the original montanic acid contained 29 carbon atoms. Note, however, that melissic acid is generally considered by most authors to contain a total of 30 carbons, not 31, as given by Kliegl, Schmid, and Merkel. Moreover, these authors specifically referred to the origin of this compound as being myricyl alcohol from bees-

wax. Beeswax, according to Conant,⁵⁴ is largely myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$. Whitmore⁵⁵ has stated that melissyl or myricyl alcohol, which has the formula $C_{30}H_{61}OH$ or $C_{31}H_{63}OH$, occurs in beeswax. If the acid considered, from the alcohol of beeswax, contained 30 carbons, then montanic acid must contain 28. The second approach to the question should carry more weight. This consisted in a Hofmann degradation of montanic acid to yield the next lower member of the series which could then be converted to an acid identical to that obtained by treating ceryl iodide (C_{26}) with sodium malonic acid ester, indicating again that montanic acid contains 29 carbon atoms.

Tropsch and Kreutzer,⁵⁶ in a series of papers, have reported in detail their findings which indicated that the montanic acid considered by others was not pure but existed as a mixture of acids. These authors subjected the methyl esters of the crude acid mixture, obtained from a middle German brown coal, to repeated fractionations at 5 millimeters pressure and temperatures ranging from 250 to 305° C. The resulting ester fractions were decomposed to the free acids, which were further purified by fractional precipitation with magnesium acetate. The purified acids were then identified by melting point and titration characteristics. It was found that the investigated material consisted chiefly of a mixture of carboceric acid, $C_{27}H_{54}O_2$ (melting point 82° C), and montanic acid, $C_{29}H_{58}O_2$ (melting point 86 to 86.5° C) which occurred in an approximate 1:1 ratio. In addition to these, small amounts of pentacosic acid ("Hyanasaure"), $C_{25}H_{50}O_2$ (melting point 78° C), were found.

⁵² Marcusson, J., and Smelkus, H. (see ref. 55), had isolated what appeared to be a mixture of saturated aliphatic alcohols (melting point 78 to 80° C) which had an average molecular weight of 356, corresponding to the formula $C_{24}H_{50}O$.

⁵³ Kliegl, A., Schmid, H., and Merkel, M., *Chem.-Ztg.*, **45**, 201 (1921).

⁵⁴ Conant, J. B., *The Chemistry of Organic Compounds*, The Macmillan Company, New York, 1934, p. 186.

⁵⁵ Whitmore, F. C., *Organic Chemistry*, D. Van Nostrand Company, New York, 1937, p. 142.

About 5 percent of the total acid mixture was thought to be melissic acid, $C_{31}H_{62}O_2$ (melting point 90 to 91° C). The montan wax was reported to exist in part as free acids (about 25 percent) and partly as esters of these selfsame acids with aliphatic alcohols.

From a Rhenish brown coal Tropsch and Dilthey⁸⁴ extracted 6.5 percent of bitumen in a Soxhlet with benzene based on the dry coal. This coal, strangely enough, gave only 3.2 percent yield with ethanol benzene (1 : 1), which is generally conceded to be a better solvent than benzene alone.⁸⁶ After saponification of the resin-free wax and purification of the various fractions, myricyl alcohol, $C_{30}H_{62}O$, and an unknown alcohol, $C_{32}H_{66}O$ or $C_{32}H_{64}O$ ("bituminol"), were obtained in a ratio 1 : 5. Carbo-ceric and montanic (C_{29}) acids were again found in a 1 : 1 ratio.

In a later paper Tropsch and Koch⁸⁵ pointed out the interesting relationship between the acids of brown coal and the acids obtained from beeswax. Gascard and Damoy⁸⁷ have reported that beeswax contains the acids $C_{25}H_{50}O_2$, $C_{27}H_{54}O_2$, $C_{29}H_{58}O_2$, and $C_{31}H_{62}O_2$, all of which, with the exception of the last, have been found in coal bitumens, and the presence of material with a molecular weight greater than that of montanic acid has been indicated. In this same paper Tropsch and Koch gave evidence indicating the presence of an acid, $C_{31}H_{62}O_2$, although there was some little discrepancy between the melting point

(88.5 to 89.0° C) which they obtained and that reported by Gascard and Damoy (90° C). The absence of the acid $C_{30}H_{60}O_2$ was established. This brings up an interesting point. Tropsch et al. were only able to isolate acids with an uneven number of carbon atoms, C_{25} , C_{27} , C_{29} , and C_{31} , and they believed that they had established the absence of acids C_{28} and C_{30} . All the acids isolated by them fit well on melting-point curves for other known acids (normal) of an uneven number of carbon atoms. Eggert,⁸⁸ however, had reported the presence of the acid $C_{26}H_{52}O_2$ in refined montan wax. Tropsch and Koch expressed the opinion that this acid was a mixture as indicated by its physical constants.

In the same year that Tropsch and Koch published their paper (1929), Holde, Bleyberg, and Vohrer⁸⁹ presented results of work which were completely contradictory to those of Tropsch et al. In this paper Holde and coworkers reported the isolation and identification of a C_{25} acid and an iso- C_{32} acid and further expressed the opinion that a C_{30} acid was probably a constituent of montan wax. They especially described montanic acid as having 28 carbon atoms and melting at 89° C. The melting point, 86.5° C, reported for the C_{29} acid of Tropsch they believed to indicate either an impure material or an iso acid. This last opinion was based on the experimental data of Levene and Taylor,⁹⁰ who have reported melting points for the normal acids (synthetic) from C_{18} to C_{26} , from which data Holde extrapolated a value of 87.88 for an n - C_{27} acid (*vs.* 82° C according to Tropsch) and 89 to 90

⁸⁶ Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **2**, 65-79 (1917), referred to a coal which gave the same yield of extract with both ether and benzene (8.67 and 8.64 percent). In general, the benzene yield is higher. A middle German brown coal gave 16.26 percent with benzene and 6.95 percent with ether. Though the second coal had a greater moisture content than the first, a better explanation of this difference probably lies in a fortuitous resin and wax ratio.

⁸⁷ Gascard, A., and Damoy, G., *Compt. rend.*, **177**, 1222-4 (1923).

⁸⁸ Eggert, F., dissertation, Halle, 1925.

⁸⁹ Holde, D., Bleyberg, W., and Vohrer, H., *Brennstoff-Chem.*, **10**, 101-8, 124-8 (1929).

⁹⁰ Levene, P. A., and Taylor, F. A., *J. Biol. Chem.*, **59**, 905-21 (1924); *Chem. Zentr.*, **95**, II, 309-10 (1924).

for an n -C₂₈ acid. Holde et al. also pointed out that earlier Fischer and Tropsch⁷¹ had stated montanic acid to contain a branched chain and that, with respect to the work of Kliegl, Schmid, and Merkel,⁸³ Tropsch himself, in a later work,⁶⁴ had referred to cerotic acid as a C₂₅ acid. Moreover, it did not appear improbable to them (Holde et al.) that both the cerotic acid and the montanic acid were impure.

Francis, Piper, and Malkin⁹¹ made a study of the higher fatty acids and pointed out several things of interest relative to the foregoing material. The problem of the higher aliphatic acids was brought to their attention in the course of an investigation of the oxidation of paraffin. The acids obtained in the process appeared to be pure normal fatty acids but differed in their properties from synthetic acids. The usual laboratory methods of purification were applied, without success, to these compounds. To gain further knowledge of the problem, a number of normal acids (up to C₂₆) were prepared by synthesis. Some of the observed properties and peculiarities of these acids were:

1. The melting points of the acids between C₁₁ and C₂₆ lay on two smooth curves; one for the odd and the other for the even acids, a well-known phenomenon. But the point corresponding to the C₂₆ acid which melted at 88.2° C was at least 0.5° C above the curve for the even acids. Levene and Taylor⁹⁰ had reported a melting point of 88 to 89° C for this acid.

2. These authors felt that there was some evidence that melting points of the acids, and particularly of those of higher molecular weight, were not entirely independent of the treatment to which they were subjected during melting. The C₂₄ acid always melted at a higher tempera-

ture when the material was in the form of finely powdered crystals than when a melted and resolidified sample was used. This difference, however, was not observed for the C₂₆ acid.

3. It was found that the melting points of equimolar acid mixtures were as sharp as those of the pure acids themselves, and, like these, the resolidification took place at a temperature within 1° C of the melting point.

4. The melting points of the mixtures, when plotted against the number of carbon atoms in the molecule, lay on a smooth curve. When the longest chain in the mixture was even, the curve was above the curve for the mixture in which the longest chain was odd.

A study made by these authors of the large crystal spacing of the pure acids, they believed, indicated that certain spacing data coupled with a correct melting point are sufficient guarantee of a high degree of purity, but neither alone is adequate. Application of this system of analysis to the products of oxidation of paraffin indicated that the products were mixtures of n -fatty acids. There was no indication of iso acids in any preparation studied. Acids of both an odd and an even number of carbons were isolated from the oxidation. The controversy existing over the names and formulas of the various higher acids is well reviewed in this paper. Montanic acid supplied by Ryan (melting point 83.6° C) gave a photograph which clearly indicated impure material, and it was thought that a mixture of acids with carbon content of either 28 and 30 or of 28, 30, and 32 existed. Another sample submitted by Holde melted at 88° C. The X-ray spacings indicated that it certainly contained C₂₈H₅₆O₂, probably in a preponderating amount, and possibly an acid of lower carbon content.

⁹¹ Francis, F., Piper, S., Malkin, T., *Proc. Roy. Soc. (London)*, **A128**, 214-52 (1930).

The effect of moisture and drying on the extraction of peat has been noted. Extractions carried out in the presence of water with benzene yielded, in general, greater amounts of bitumens. This same effect has been reported for brown coal. The Soxhlet extraction of a Bohemian brown coal with benzene gave a yield of 1.2 percent for a sample dried at 105° C and 2.2 percent with the undried (10 to 20 percent water) material.⁹² Later Fischer and Schneider⁹³ studied the effect of water on the Soxhlet and pressure extraction of brown coal. The yields of extract with benzene from the atmospheric extractions are given in Table XI. It can

TABLE XI

EFFECT OF MOISTURE ON YIELD OF EXTRACT FROM BROWN COALS⁹³

	Dried at 105° C	Air Dried, about 10 Percent Water	Dried at 105° C and Water Added
Middle German brown coal I	11.5	15.5	14.2
Middle German brown coal II	11.1	14.9	14.4
Niederlausitz brown coal	11.1	14.0

be seen that readdition of water to the dried coal restored the value of the yield to almost the figure obtained with the moist material. This was not true with peat. When the extractions were carried out on one of the brown-coal samples at 240 to 245° C with benzene the total yield was 23.8 percent for the coal dried at 105° and 31.2 percent for the same coal dried at 105° C but remoistened with water. The fact that the increased yield was not due to the solution of humic acids was established by the insolubility of both extracts in an alkaline solution.

Just as with peat, extractions carried out

⁹² Schneider, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 150-63 (1918).

⁹³ Fischer, F., and Schneider, W., *ibid.*, **3**, 315-24 (1918).

under pressure with benzene result in an increase in yield over atmospheric extraction. Some light has been thrown by Fischer and Schneider⁹⁶ on the mechanism by which such an increase is obtained. In the first of two experiments, 20 grams of residue from an exhaustive extraction with benzene at atmospheric pressure was heated for 1 hour at 250 to 260° C. At the end of this period, the remaining material (18.1 grams) was extracted with benzene in a Soxhlet (atmospheric) giving a yield of 0.27 percent. In the second experiment the raw coal (15 grams) was treated in a similar manner. The residue (10 grams) as before was extracted with benzene, yielding 3.1 percent bitumens. The coal used in these experiments was brown coal Union-Briquettes (12.5 percent moisture), which, upon extraction with benzene, gave yields of: 3 to 3.5 percent in a Soxhlet, 4.4 percent at 150° C, and 7.2 percent at 220 to 250° C. It would, therefore, appear that the increased yield at the higher temperature was not the result of thermal breakdown to give more soluble products, but rather an ordinary solution phenomenon. The decrease in weight of the coal sample upon heating was due to loss of water, about half of which was the original moisture content. Some hydrogen sulfide was lost, but very little organic material (oillike material). In the same paper data were presented for another brown coal (Saxon) which gave a yield of 11 percent in a Soxhlet and 25 percent at 260° C.

In a later paper² it was shown that, if the residue from the Soxhlet extraction of Union-Briquettes with benzene was heated to 250° C in the presence of a small amount of benzene and then subsequently extracted with this same solvent in a Soxhlet, the yield was 0.47 percent. These authors pointed out that the observations

in the preceding paper were not true for all coals. It was found that a mid-German brown coal which gave 11 percent bitumen A and 14 percent bitumen B at 250° C (total 25 percent) yielded an additional 8 percent of bitumens after the previously extracted coal had been heated to 250° C. When the coal residue was heated to 250° C in the presence of a little benzene, the yield of extract upon atmospheric Soxhlet extraction was 15 percent. Another brown coal (Riebeck Montanwerke) yielded 13.6 percent extract A and 5.35 percent extract B. When the bitumen-A-free coal was heated to 250° C and then extracted as before, 1.15 percent yield was obtained. Heating the same residue to 250° C in the presence of a small amount of benzene and subsequent extraction in a Soxhlet yielded 5.35 percent additional bitumen.

Data have been presented from time to time on the effect of dilute acids on the yield of extract. Little information is available on the conditions of such treatment, nor are there many data on the variations of bitumen C content of different coals. Several authors⁹⁴ have reported that increases of 60 to 90 percent of ethanol-benzene extract were obtained after treatment of brown coal with dilute hydrochloric acid. Hock and Engelfried found that the temperature of treatment (20 to 115° C) was not a factor in increasing yield. The C bitumens did not soften or melt but decomposed, and their volatile matter was markedly less in amount than that of the A bitumens, whereas their acid and saponification numbers were much greater. An attempt to decompose organic salts without removal of the ash with gaseous sulfur dioxide was only partially successful.

⁹⁴ Grün, A., and Ulbrich, E., *Z. deut. Öl- u. Fett-Ind.*, **40**, 773-5 (1920); *Chem. Abs.*, **15**, 744 (1921). Hock, H., and Engelfried, O., *Braunkohle*, **37**, 161-5 (1938).

Yields of extract from so-called synthetic coals have been reported, but the amount of available data is not sufficient to establish any general statements. Terres⁹⁵ has reported that sphagnum peat, when heated to 280 to 300° C for 20 hours, gave a material resembling brown coal which, upon extraction, yielded 35 percent of a viscous black oil. Bode⁹⁶ reported a decrease in ethanol : benzene-soluble material when brown coal was heated to 300 to 520° C under compression to produce varying degrees of coalification.

Trifonov and Toshev⁹⁷ reported the effect of pressure (10,000 kilograms per square centimeter) on three brown coals, a bituminous humus coal, and three low-volatile and three high-volatile bituminous coals. It was found that a considerable reduction of the amount of benzene-soluble material (bitumen A) was obtained after compression. The authors did not state whether or not the compressed material was broken up before extraction. If it was not broken there is a great possibility that material so obtained would be impervious to the solvent. Changes were also observed and reported in the yield of tar, oils, and low-temperature coke, in the state of the sulfur content, and in the actual specific gravity of the coal and its coke.

Stadnikoff⁹⁸ described a young sapropelic coal (balchaschite) which, upon successive Soxhlet extraction with benzene, benzene, and alcohol, yielded 15.2, 4.1, and 4.2 percent extract or a total of 23.5 percent. This coal is indicated by its analysis to fall outside the coal band⁹⁹ (C 73.76,

⁹⁵ Terres, E., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 797-808 (1931).

⁹⁶ Bode, H., *Braunkohle*, **36**, 87-90 (1937).

⁹⁷ Trifonov, I., and Toshev, G., *Brennstoff-Chem.*, **20**, 128 (1939); **21**, 85-7 (1940).

⁹⁸ See p. 123 of ref. 3 and Chapter V of ref. 4.

⁹⁹ Stadnikoff, G., and Falkowskaja, A., *Brennstoff-Chem.*, **16**, 381-2 (1935), stated that while humus coals consist of bitumens and humus ma-

H 10.91, S 1.03, N 0.56, and O 13.74 per cent respectively).

Another sapropelite (boghead coal)⁹⁸ higher in rank gave a much lower yield of bitumens as a result of polymerization of the resin and wax material and through the formation of a dehydration product of the acids. The unpolymerized chemical compounds, according to Stadnikoff, were high-molecular-weight, saturated, monobasic acids, and their anhydrides. The yields and properties of the A and C bitumens¹⁰⁰ are given in Table XII. The

numbers). The presence of free double bonds was indicated by the increased iodine value. Stadnikoff also believed that the lower hydrogen content of the C bitumen indicated the presence of substances with two and three double bonds.

The A bitumen of this coal was separated with hot and cold alcohol-benzene into four fractions. Further separation was made with benzene, benzene, and alcohol. The benzene-soluble material contained 11.3 percent unsaponifiable material with a very low iodine number (about 4) and

TABLE XII

COMPARATIVE DATA FOR BITUMENS A AND C FROM BOGHEAD COAL⁹⁸

Chachareisky ¹⁰¹ Boghead Coal	Bitumen A						Bitumen C					
	Melt- ing	Acid	Saponifi-	Iodine	Carbon	Hydro- gen	Melt- ing	Acid	Saponifi-	Iodine	Carbon	Hydro- gen
	Point percent °C	Num- ber	cation Number	Num- ber			Point percent °C	Num- ber	cation Number	Num- ber		
Stratified (1)	8.3 70-75	60	111	13.0	78.3	12.4	2.4 85-90	153	314	46.5	65.9	7.5
Compact	5.7 69-76	62	99	17.7	78.1	12.2	0.7 ca. 126	121	239
Stratified (2)	3.7 75-80	56	87	12.1	77.1	12.0	4.4 78-88	97	246	17.2	66.1	9.1
Shale coal	4.8 78-80	56	104	21.9	79.2	12.0	1.9 90-95	115	277	51.7	67.9	8.3

A bitumens of this coal were reported to consist chiefly of a mixture of high-molecular-weight unpolymerized fatty acids, as was indicated by the low melting point, low iodine and saponification values, and high hydrogen content of the bitumens. The C bitumens were thought to be polymerized unsaturated fatty acids of average molecular weight, indicated by the high saponification number. About half of the carboxyl of these acids existed as anhydride (based on the saponification and acid

no hydroxyl groups. This hydrocarbon mixture was crystallized from alcohol yielding three fractions, two of which on the basis of analysis and melting were thought to be $C_{31}H_{64}$ and $C_{34}H_{70}$. These hydrocarbons made up 1.5 percent of the A bitumen. It should again be pointed out that analysis of such high-molecular-weight material is of questionable value in determining empirical formulas, nor can too much significance be attached to the melting points.

terial, the sapropelic coals are made up of fatty acids and their degradation products. The low temperature tar from sapropelic coal contains no phenol.

¹⁰⁰ The author did not state (*Die Chemie der Kohle*) with which solvents these bitumens were obtained.

¹⁰¹ Additional data for similar coals, bitumens A, B, and C, are given by Stadnikoff, G., and Wöhner, R., *Brennstoff-Chem.*, 12, 23-5 (1931).

Bitumen B was obtained from this coal in amounts ranging from 1.0 to 3.3 percent and melted at 40 to 57° C. The low melting point, together with the high hydrogen and carbon content of the extract, was believed to indicate that this material had originated in the degradation of the C bitumen through splitting out of carboxyl

groups.¹⁰² The iodine numbers of the B and C bitumens were almost identical and indicate that only decarboxylations were involved in the transformation.

Sapropelic coal of the Kuznetz basin¹⁰³ upon extraction at atmospheric pressure with ethanol, acetone, chloroform, gasoline, ether, and benzene yielded a maximum of 3.8 percent bitumens on a dry, ash-free basis. The analysis of this coal indicates that it is almost pitchlike in nature.

Matogan sapropelite,¹⁰⁴ when extracted in an autoclave for 6 to 7 hours at 240 to 250° C with tetralin, yielded 18.3 percent of soluble material based on the weight of the coal. The extract contained 11.85 percent ash and 66.5 percent resins. The wax-like part contained acids of low molecular weight: acetic, oleic, and valeric, which were probably produced in the extraction through thermal degradation. High-molecular-weight acids were also found, one of which was believed to contain 32 carbon atoms.

Solvents other than benzene and ethanol-benzene have been used in the extraction of brown coal.¹⁰⁵ Donath⁴⁴ used a

¹⁰² Kerenyi, B., *Braunkohle*, **30**, 508-13, 529-36 (1931), also pointed out that the low oxygen content of brown-coal bitumen B is probably the result of a condensation process.

¹⁰³ Karavaev, N. M., *Fuel*, **13**, 299-310 (1934).

¹⁰⁴ Rakovskii, E. V., and Mamontova, O. M., *Khim. Tverdogo Topliva*, **5**, 230-4 (1934); *Chem. Abs.*, **28**, 7481 (1935).

¹⁰⁵ Erdmann, E., and Dolche, M., *Die Chemie der Braunkohlen*, W. Knapp, Halle (Saale), 1927, p. 118, tabulated the results obtained in the atmospheric extraction of a large number of brown coals with benzene. For additional work on benzene and ethanol-benzene extractions see Smith, W., *J. Soc. Chem. Ind.*, **17**, 985-8 (1898). Marcusson, J., *Chem. Rev. Fett- u. Harts-Ind.*, **15**, 193-5 (1908); *Z. angew. Chem.*, **40**, 1104-6 (1927). A. Riebeck'sche Montanwerke, Ger. Pat. 305,349 (1916), 325,165, (1919). Bube, K., *Jahrb. Halleschen Verbandes Erforschung mitteldeutschen Bodenschätze*, **2**, 229-39 (1920). Schellenberg, A., *Brennstoff-Chem.*, **1**, 73-5 (1920). Fellicola, P., *Giorn. chim. ind. applicata*, **3**, 546-8 (1921); *Chem. Abs.*, **16**, 2589 (1922). Erdmann, E., *Z. angew. Chem.*, **34**, 309-14

mixture of benzene and acetone, and Schneider⁵⁴ has shown a mid-German brown coal to be 7.6 percent soluble in acetone. Reextraction of the residue with benzene gave an additional yield of 5.4 percent of extract or a total yield of 13 percent. The original coal was 14.2 percent soluble in benzene; the difference was probably due to oxidation on handling. References to the use of other organic solvents and solvent mixtures for brown-coal and lignite extraction and hydrogenation¹⁰⁶ are quite numerous in the litera-

(1921). Pschorr, R., Pfaff, J. K., and Berndt, W., *ibid.*, **34**, 334-6 (1921). Meneghini, D., *Giorn. chim. ind. applicata*, **4**, 203-4 (1922); *Chem. Abs.*, **16**, 2589 (1922). Piening, B., *Braunkohle*, **22**, 481-4, 505-11 (1923). Tropisch, H., *Brennstoff-Chem.*, **5**, 369-74 (1927). Mailhe, A., *J. usines gaz*, **51**, 187-8 (1927); *Chem. Abs.*, **21**, 2548 (1927). Fuchs, W., *Brennstoff-Chem.*, **11**, 205-8 (1930). Vener, R. A., *Khim. Tverdogo Topliva*, **5**, 200-9 (1934); *Chem. Abs.*, **29**, 316 (1935). Kuznetsov, V. I., and Rominskii, I. P., *Mem. Inst. Chem. Tech. Ukrain. Acad. Sci. U.S.S.R.*, No. **1**, 13-52 (1936). Kuznetsov, V. I., and Trofimovskii, N. S., *ibid.*, No. **1**, 53-9 (1936); *Chem. Abs.*, **31**, 5131-2 (1937). Priman, M., *Acta Univ. Latviensis, Kim. Fakultät. Ser.*, **3**, Nos. 5-8, 229-309 (in German 31-14) (1936); *Chem. Abs.*, **31**, 5132 (1937). Voitova, E. V., *Brennstoff-Chem.*, **17**, 201-3 (1936). Titov, N. G., and Fedoseeva, S. F., *Khim. Tverdogo Topliva*, **8**, 793-803 (1937); *Chem. Abs.*, **32**, 2324 (1938). Veisel'berg, K. B., and Babenko, E. M., *Ukrain. Khim. Zhur.*, **12**, 87-90 (1937); *Chem. Abs.*, **31**, 5132 (1937).

¹⁰⁶ ACETONE: Hodurek, R., *Oesterr. Chem.-Ztg.*, **7**, 365-70 (1904). ANTHRACENE OIL: Scheithauer, W., *Braunkohle*, **3**, 97-104 (1904). D'yakova, M. K., Lozovoi, A. V., Stepankova, T. G., and Senyavin, S. A., *Compt. rend. acad. sci. U.R.S.S.*, **20**, 681-4 (1938) (in English); *Chem. Abs.*, **33**, 3561 (1939). PETROLEUM ETHER: Roderer, W. R., Ger. Pat. 640,522 (1930). Soltys, A., *Monatsh.*, **53/54**, 175-84, 185-6 (1929). BENZENE-ACETONE: A. Riebeck'sche Montanwerke, Ger. Pat. 325,165 (1919). BENZENE-WATER AND TOLUENE-WATER INSOLUBLE PART OF FUSEL OIL: A. Riebeck'sche Montanwerke, Ger. Pat. 386,435 (1932). BENZENE-METHANOL: Cropp, J., and Knott, G., Ger. Pat. 509,813 (1929). HIGH-BOILING TAR FRACTIONS AND PETROLEUM OIL: Rose, H. J., and Hill, W. H., Eng. Pat. 356,239 (1929). HYDROCARBONS, ALCOHOLS, ETHERS, CY-

ture, both alone and in the presence of catalytic materials, and occasionally even inorganic compounds have been used. Sulfur dioxide as the liquid⁴⁹ and dissolved in acetone⁵⁰ have already been mentioned. Fischer and Gluud found that even anthracites were disintegrated to a fine powder by sulfur dioxide. Cannel coal, however, was only slightly affected; the addition of water to the sulfur dioxide solution brought about the separation of a heavy oil which, upon steam distillation, yielded a yellow oil

CYCLOHEXANOL, AND CYCLOHEXANONE: Hamburger, S., Ger. Pat. 367,330 (1920). PETROLEUM ETHER AND ACETONE (AFTER PRELIMINARY TREATMENT OF THE COAL WITH ALKALI): Hamburger, S., Ger. Pat. 367,330 (1920). Roederer, W. R., Ger. Pat. 640,522 (1930). HYDROGENATED OILS, ACID OILS, AND TETRALIN-CRESOL MIXTURES: Gewerkschaft Mathias Stinnes, Fr. Pat. 805,840 (1936). METHYL ALCOHOL OR CYCLOHEXANOL: A. Riebeck'sche Montanwerke, Ger. Pat. 583,872 (1937). NAPHTHALENE: Kohler, H., Ger. Pat. 204,256 (1906). TETRALIN: Ubaldini, I., and Mariotti, A., *Atti X^e cong. intern. chim.*, **3**, 665-73 (1939); *Chem. Abs.*, **33**, 8960 (1939). Levi, M. G., and Winter, H., *Brennstoff-Chem.*, **20**, 144-7. Sandor, A., *Anales asoc. quim. argentina*, **20**, 51-71 (1932); *Chem. Abs.*, **26**, 5729 (1932). Sinnes, H., Ger. Pat. 411,440 (1922). TETRALIN-PHENOLIC TAR FRACTIONS: Meyer, H., and Nicoud, K., Ger. Pat. 663,391 (1937). PYRIDINE: Péter, I., *Szénkísérleti Közlemények*, **2**, 71-75 (1927); *Chem. Abs.*, **24**, 3627 (1930). SOLUTION OF COAL AND HYDROGENATION OF THE EXTRACTS: Levi, M. G., and DeBartholomaeis, E., *3rd. congr. int. carbonio. carb.*, September, 1937, *Studi ric. comb.*, **6**, 259 (1936-7). D'yakova, M. K., Lozovoi, A. V., and Kardasevich, V. P., *J. Applied Chem. (U.S.S.R.)*, **12**, 545-53 (in French, 554) (1939). D'yakova, M. K., and Senyavin, S. A., *ibid.*, **12**, 555-62 (1939); *Chem. Abs.*, **33**, 8384 (1939). HYDROGENATED OILS, TETRALIN, ETC., MIXED WITH PHENOLS, PHENOLIC OILS, TAR FRACTIONS, ETC., UNDER A PRESSURE OF HYDROGEN IN THE PRESENCE OF MOLYBDIC ACID AS A CATALYST: Gewerkschaft Mathias Stinnes, Fr. Pat. 797,264 (1936). THE ADDITION OF HYDROGENATED CYCLIC HYDROCARBONS, THEIR DERIVATIVES SUCH AS AMINES AND SATURATED AMMONIA SOLUTION IN ALCOHOL TO THE EXTRACTION SOLVENT (C₆H₆): Nast, H., Ger. Pat. 541,829 (1928). THE ADDITION OF SUFFICIENT ACID (H₂SO₄) TO NEUTRALIZE THE BASIC CONSTITUENTS OF COAL (PREFERABLY LIGNITES) AND THE USE OF A WETTING AGENT SUCH AS DI-BUTYLNAPHTHALENE SULFONIC ACID: I. G. Farberind. A.-G., Fr. Pat. 811,367 (1937).

having a faint petroleumlike odor. Lenher¹⁰⁷ found that selenium oxychloride would extract up to 20 percent of "bituminous" materials from coals of higher rank than lignite.

Berl and Schmid¹⁰⁸ studied the effect of chloroform, benzene, decalin, and tetralin on oil shales. These authors were among the first to recognize the superior nature of tetralin as a solvent.¹⁰⁹ The extraction of German brown coal yielded 7.2 percent extract with boiling benzene and 9.6 percent extract under pressure (about 220° C). The same coal extracted with tetralin gave 9.3 percent at the boiling point and 18.2 percent in a pressure extraction. The extractions at the boiling point cannot be compared since such a great difference exists in the two temperatures, but the results at 220° C are striking. Note here that the partial pressure of hydrogen over tetralin has been given by Maillard¹¹⁰ as about 0.79 atmosphere at 220° C and 1.16 atmospheres at 250° C. These authors found that 16.9 percent of Bohemian brown coal could be extracted with tetralin at the boiling point and 37.4 percent at about 250° C. This last yield was for a single extraction of 5 hours, using 50 grams of dried coal and 500 cubic centimeters of solvent in an autoclave. All yields were calculated to the dry-coal basis. Extraction of this same coal at atmospheric pressure gave a 16.9 percent yield. The tetralin pressure extract was distilled at 30 millimeters pressure, 60.6 percent being volatile below 300° C. The fraction boiling in

¹⁰⁷ Lenher, V., *Engineering*, **110**, 210 (1920); U. S. Pats. 1,385,081 (1921), 1,445,329 (1923).

¹⁰⁸ Berl, E., and Schmid, W., *Brennstoff-Chem.*, **7**, 49-54, 181 (1926).

¹⁰⁹ Earlier H. Novak had shown that tetralin was an excellent solvent both at the boiling point and under pressure (above 300° C), *Paliva a Topeni*, **5**, No. 2 (1923).

¹¹⁰ Maillard, A., *Ann. combustibles liquides*, **9**, 1013-70 (1934), **10**, 95-139 (1935).

the range 200 to 300° C was divided into neutral oils, 88 percent, and alkali-soluble acids and phenols, 11.6 percent, of which 83 percent could be precipitated with carbon dioxide.

Further extractions made on Cassel brown coal with benzene and tetralin at the boiling point and at about 220° C gave the following results:

- I. (a) 2.8 percent yield with benzene at atmospheric pressure (4 hours).
- (b) 4.6 percent yield with benzene at 210° C (2 hours).
- II. (a) 5.2 percent yield with tetralin at atmospheric pressure (4 separate half-hour extractions).
- (b) 12.7 percent yield with tetralin at 220° C from the extraction of the residue from II(a) (2.5 hours).
- (c) 3.9 percent yield with tetralin at 220° C from the extraction of the residue for II(b) (4 hours).

After extractions II(b) and II(c), the residue was washed four times with additional tetralin. The total extract by this entire process (II) was 21.8 percent against 22.2 percent obtained in two successive extractions with tetralin at 220° C (III).

TABLE XIII

ACID AND ESTER NUMBERS OF TETRALIN EXTRACTS FROM CASSEL BROWN COAL¹⁰⁸

		II(b)	II(c)	III
Acid number	36.6	53	61.3	78.0
Ester number	74.0	75.1	48.2	148.5
			153.0	

The acid and ester numbers of the various extracts are shown in Table XIII. Note the similarity between I(a) and II(a) and the fact that they both agree with the values given earlier for montan wax. The high ester number of the last two extractions might indicate that a large part of the extract consisted of resins. Analyses of the products from the pressure tetralin extractions are given in Table XIV. Data were also presented which indicated that the tar obtained in distillation and the extract had their origin in the same coal constituents. Distillation of the extracted coal yielded only a small amount of tar. Similar results have been reported elsewhere.¹¹¹ The extract from the first and second tetralin extractions was found to contain 17.3 percent of material insoluble in ether and 3.4 percent insoluble in benzene. Further subdivision of this extract was made with petroleum ether, ethyl ether, benzene, 20 percent sulfuric acid, and 5 percent sodium hydroxide to give amorphous powders, resins, waxes, pitch, and oils.

Novak and Hubaček¹¹² extracted two Czechoslovakian brown coals from the

¹¹¹ Graefe, E., *Die Braunkohlenteerindustrie*, W. Knapp, Halle, 1906, p. 9. Scheithauer, W., *Die Schmelteere: Ihre Gewinnung und Verarbeitung*, O. Spamer, Leipzig, 1911, p. 145.

¹¹² Novak, H., and Hubaček, J., *Paliva a To-pení*, 9, 185-7 (1927), 10, 3-9, 22-8, 28-33, 41-51 (1928).

TABLE XIV

ANALYSIS OF PRODUCTS FROM TETRALIN EXTRACTION OF BROWN COAL¹⁰⁸

	Percentage Composition on Dry Basis			Percentage Composition on Dry, Ash-Free Basis		
	Ash	Carbon	Hydrogen	Carbon	Hydrogen	Oxygen
Coal	9.7	52.47	4.63	58.12	5.13	36.75
Coal residue after two extractions	14.0	54.26	4.38	51.12	3.93	44.95
Coal residue after three extractions	15.6	54.74	4.41	50.28	3.79	45.96
Tetralin extract II(a) and (b)				82.52	8.81	8.67
Tetralin extract II(c)				76.10	6.79	17.11

Karolina and Hedvika seams (both in northern Bohemia) with tetralin and obtained yields of 26 and 24 percent on a dry, ash-free basis. Both coals were extracted for 8 hours at 300° C.

These papers are of great importance in the field of solvent extraction. In the introduction of the use of tetralin they have served as a nucleus for a considerable number of investigations of the extraction of bituminous coals with this powerful solvent. Tetralin alone and mixed with other solvents is being used abroad today in the large-scale hydrogenation of coal, and in this country to a small extent in experimental installations. The action of tetralin as a dispersion medium in the hydrogenation of coal is threefold: first, it is an excellent solvent itself; second, it serves to reduce the viscosity of the material to be hydrogenated; and third, it serves as a "hydrogen carrier." Since the coal extracts commercially obtained abroad with such solvents as tetralin and tetralin-phenol mixtures are low in ash content, they have found use in the aluminum industry as a source of electrode carbon.

A great deal of the work described in the previous pages was carried out with apparent disregard of many factors important in solvent extraction. Authors have referred vaguely to coal size as small lumps, crushed, nut size, etc., or have arbitrarily picked a temperature to carry out extractions without first investigating the important variable of temperature. Extractions have often been made in such a short period of time that complete removal of all soluble material hardly seems possible. Soxhlet extractions are often stopped when the liquid siphoning is no longer highly colored, although it can be shown that some material is still being removed even when the solvent is apparently colorless. Those workers who have used beakers, tin cans,

or bombs could hardly have reached the completeness of extraction attained in a Soxhlet, either pressure or atmospheric. In this connection it should be pointed out that Soxhlet extraction, though theoretically perfect, often actually is not, owing to channeling of the fresh solvent through the material in the thimble. Often non-soluble material such as glass or sand is admixed with the substances in the thimble to prevent this.

In recent years more attention has been paid to the variables of solvent extraction. Jostes and Siebert¹¹³ have published one of the few papers on brown coal in which these important variables are considered. These authors investigated the effects of time, temperature, and solvent on the yield of extract and on the chemical nature of the extraction products. The yield of extract was found to increase with time, over the period studied, but no attempt was made analytically to study the data obtained except to point out that the extraction curve was not parabolic. Increases in temperature were also found to increase the yield up to the highest temperature studied (370° C). Present-day knowledge of the coal extraction process would indicate that, at a temperature above this, the yield should go through a maximum region and then actually decrease with further increases in temperature. Insufficient data were presented to show that the extraction of this particular coal would follow such a course. The extractions, eleven in number, were made in an electrically heated bomb which unfortunately had no provision for stirring or mixing the contents. The coal extracted was an upper Hessian brown coal, high in moisture, ash, and bitumen content,¹¹⁴ ground to pass a 900

¹¹³ Jostes, F., and Siebert, K., *Oel, Kohle, Erdoel, Teer*, **14**, 777-83 (1938).

¹¹⁴ Scheerer, B., *Braunkohle*, **13**, 393-5 (1914). Sander, A., *Brennstoff-Chem.*, **10**, 21-6 (1929).

mesh per square centimeter (70 mesh per inch) sieve. The analysis of the coal is shown in Table XV. The solvent used consisted of tetralin in crude cresol ($d = 1.0345$ or $d = 1.033$).

TABLE XV

PERCENTAGE COMPOSITION OF AN UPPER HESSIAN BROWN COAL ¹¹³

	Raw Coal	Air- Dried	Water- Free	Dry, Ash-Fr
Water	57.4	29.0		
Volatile matter	20.5	34.2	48.2	71.3
Fixed carbon	8.3	13.8	19.4	28.7
Ash	13.8	23.0	32.4
Carbon		32.5	45.8	67.8
Hydrogen		2.7	3.8	5.6
Nitrogen+oxygen		12.2	17.2	25.5
Sulfur		0.426	0.6	0.9

The various runs were made by charging 20 grams of the air-dried coal and 100 grams of the solvent mixture into the bomb, which was subsequently heated to the desired temperature. The heating time necessary to reach the reported temperature was about 50 to 80 minutes. This period of time is not included in the extraction time given in the table. The material removed from the bomb was centri-

fuged at 2,500 to 3,000 rpm for 20 minutes to separate the extract and residue. The residue was washed once with fresh solvent and three times with acetone, the washings were combined with the first material (extract) removed in the centrifuging, and the solvent was distilled off, leaving the dry extract. The experimental conditions and results are shown in Table XVI. Several things in this table and in the original article are of interest:

1. A solvent balance was given which indicated that an average of 94 percent of the original material was recovered.

2. The extract yields given in the sixth and seventh columns were calculated by the method of Parr and Hadley ¹¹⁵ as the difference between the moisture-free weight (14.2 grams) of coal and the dried residue, or, in other words, on the basis of the residue.

3. The percent yields were reported on the basis of the dry, ash-free coal.

4. The average difference between the yield calculated on the basis of the residue

¹¹⁵ Parr, S. W., and Hadley, H. F., *J. Soc. Chem. Ind.*, **34**, 213 (1915); *Fuel*, **4**, 31-8, 49-55, 111-8 (1925).

TABLE XVI

CONDITIONS OF EXTRACTION AND YIELD OF EXTRACT FROM HESSIAN BROWN COAL ¹¹³

Experi- ment Number	Extraction Tem- perature °C	Time of Ex- traction hours	Tetralin Content of Solvent percent	Residue grams	Extract, Calculated		Extract, Obtained	
					grams	percent	grams	percent
1	275	1	10	8.88	5.32	55.4	5.37	56.0
2	300	1	0	8.28	5.92	61.7	6.01	62.6
3	300	1	10	8.30	5.90	61.5	5.96	62.1
4	300	1	20	8.31	5.89	61.4	5.97	62.2
5	300	1	30	8.28	5.92	61.7	6.01	62.6
6	325	1	10	7.80	6.40	66.7	6.50	67.7
7	350	1	10	6.62	7.58	79.0	7.70	80.2
8	350	3	10	6.00	8.20	85.5	8.35	87.0
9	350	6	10	5.53	8.67	90.4	8.84	92.2
10	350	9	10	5.46	8.74	91.0	8.95	93.2
11	370	1	10	5.99	8.21	85.5	8.41	87.5

and on the basis of the original coal was about 1.6 percent.

The influence of temperature on yield (experiments 1, 3, 6, 7, and 11) is shown in Fig. 1. The curve as drawn indicates that there might be a maximum in the neighborhood of 400° C. Although insufficient data were presented to indicate this, such a maximum would be in agreement

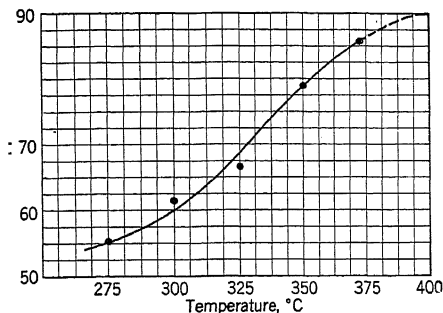


FIG. 1. Influence of extraction temperature on yield of extract with tetralin-cresol mixture as solvent; time of extraction, 1 hour.^{11,12}

with the findings of Pott, Broche,^{11,12} and others who have carried out similar extractions. Pott, Broche, et al. showed that for each coal there was a definite temperature of extraction where a maximum yield of extract was obtained. Above this temperature, a decrease in the amount of soluble material obtained was observed. This optimum temperature, according to Pott, Broche, et al., was just below the decomposition temperature of the residue. Hence, if a maximum yield is to be obtained the extraction must be carried out in stages in which the residue from each extraction is reextracted at a higher temperature with fresh solvent since the decomposition temperature of the residue increases, to some constant value, upon successive extractions.

^{11,12} Pott, A., Broche, H., Nedelmann, H., Schmitz, H., and Scheer, W., *Glückauf*, **69**, 903-12 (1933); *Fuel*, **13**, 91-5, 125-8, 154-7 (1934).

It was pointed out^{11,12} that the extraction process involves not only a physical solution of material but also a chemical decomposition or depolymerization of the coal substance. Reference was also made to the possibility of chemical combination between the solvent and coal substance. The amount of depolymerization was believed to decrease with cooling and to increase with increases in temperature so that at each temperature an equilibrium was established between polymerization and depolymerization processes. In addition to the possibility of repolymerization upon cooling, which was not experimentally confirmed, a definite tendency was observed for the extracts to repolymerize in

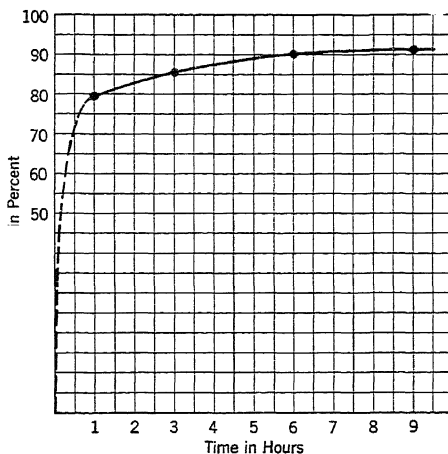


FIG. 2. Influence of extraction time on yield of extract with tetralin as solvent at 350° C.^{11,12}

the presence of light, forming insoluble material.

The effect of time of extraction as indicated by experiments 7, 8, 9, and 10 is shown in Fig. 2 and in Table XVI. The extraction process was divided by Jostes and Siebert into four different steps: (1) the penetration of the solvent into the coal particles; (2) the loosening up of the

molecular bindings of the coal substance; (3) the depolymerization of larger molecular aggregations; and (4) the diffusion of the bitumens from the coal into the solvent.

Earlier, Keppeler and Borchers¹¹⁷ had reported that the extraction curve, as a result of the process being one of diffusion, took the shape of a parabola. Peters and Cremer¹¹⁸ also pointed out that the extraction of μ -coal with benzene and trichloroethylene followed a parabolalike course for a while. It was found, by these authors, that the amount of extract declined as $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4} \dots 1/n$ when the extraction time was lengthened 2, 3, 4 $\dots n$ times, so that the extraction velocity was a hyperbolic function of time according to the formula $\frac{dE}{dt} = \frac{K}{t}$, in which dE is the amount of bitumen extracted in the time dt and K is a constant.

On the basis of the foregoing experiments, Jostes and Siebert calculated the constants K and c (equation of parabola, $E^2 = ct$) given in Table XVII. From these

TABLE XVII

EFFECT OF TIME ON EXTRACTION YIELDS AT 350° C¹¹³

Experiment number	7	8	9	10
Time in hours	1	3	6	9
Yield in percentage, E	79.0	85.5	90.4	91.0
$c = \frac{E^2}{t}$	6,241	2,437	1,362	920
$\frac{dE}{dt}$, grams per hour	79	3.25	1.63	0.2
$\left(\frac{dE}{dt} t\right)$	79	9.75	9.80	1.80

data and Fig. 2 it can be seen that the extraction curve is not parabolic. If the ideal extraction curve is parabolic,¹¹⁹ then

¹¹⁷ Keppeler, G., and Borchers, H., *Brennstoff-Chem.*, **15**, 241-5, 404-5 (1934).

¹¹⁸ Peters, K., and Cremer, W., *Angew. Chem.*, **47**, 576-8 (1934).

¹¹⁹ Tammann, G., *Z. anorg. allgem. Chem.*, **111**, 78-89 (1920). Keppeler, G., and Thomas, M.,

deviations indicate that the coal substance contains materials which either have different solubilities or differ in rate of depolymerization. There can be no doubt that brown coals contain considerable amounts of substances which occur merely as occluded material. The removal of these easily soluble bitumens by extraction in a Soxhlet with a low-boiling solvent before the pressure extraction should materially influence the shape of the curve in Fig. 2.

The extractions carried out with solvents in which the tetralin content ranged from 0 to 30 percent (300° C runs 2, 3, 4, and 5) gave identical yields. Hence, the solvent power of the mixture would seem to lie entirely in the cresol. It is interesting to note with respect to these experiments that, whereas the hydrogen balances remain about the same for runs 2 to 5, the percentage of hydrogen in the extract increased with increased tetralin content of the solvent. This increase appears to take place at the expense of the hydrogen in the residue. The opinion has been expressed that the tetralin serves not only to reduce the viscosity¹²⁰ of the coal solution but also to stabilize unsaturated fragments of the coal substance.

To point out the influence of experimental conditions, analytical data for carbon, hydrogen, and ash in the extract and residue were reported. The following general statements can be made:

1. The ash content of the extract varied from 5.1 to 6.1 percent. Though the question of inadequate separation by centrifuging was raised, it was thought to be offset by the fact that the ash content increased with the temperature of extraction and that the extract solution after centrifuging appeared to be homogeneous. The possibility

Glastech. Ber., **11**, 205-8 (1933); *Chem. Abs.*, **27**, 5497 (1933).

¹²⁰ Piatti, L., *Angew. Chem.*, **47**, 732-3 (1934).

of colloidal suspension was not investigated. At any rate, only 6 to 11 percent of the ash of the original coal appeared in the extract, 89 to 94 percent remaining in the residue. The possibility of a reaction between the cresol and the ash was mentioned.

2. The carbon content of the ash-free extract ranged from 73.3 to 77.2 percent and exceeded that of the dry, ash-free coal by an average of 7.5 percent.

3. The hydrogen content of the extract averaged 0.65 percent above that of the dry, ash-free coal and tended to decrease with increasing temperature from 6.7 to 5.9 percent.

4. The ash content of the residue increased with temperature from 48.9 (275° C) to 68.3 percent (370° C). Increasing the extraction time from 1 to 9 hours increased the ash content of the residue from 62.5 to 74.5 percent.

5. The carbon content of the ash-containing residue ranged from 29.6 to 10.6 percent and decreased with increasing temperature and time of extraction, as did the carbon content on a dry, ash-free basis (58.0 to 41.7 percent).

6. The hydrogen content of the ash-containing residue (2.16 to 1.05 percent) decreased with increasing temperature, time of extraction, and increasing tetralin content of the solvent. On an ash-free basis (4.66 to 4.04 percent), however, a change with temperature alone was not evident except that there was a sudden jump at 350° C, which was about 0.21 percent higher than the value at higher and lower temperatures.

7. The amount of volatile matter in the residue decreased with increasing temperature and time of extraction. Between 275 and 370° C it fell from 48.6 to 26.2 percent and at 350° C from 33.3 (1 hour) to 19.7 percent (9 hours). The residue from the

volatile-matter determinations was principally ash and contained only about 3 to 4 percent carbon. On a dry basis the original coal contained 48.2 percent volatile matter.

A second paper by these authors¹²¹ dealt with the possibility of using brown-coal extracts as a solid fuel for internal-combustion engines.

The effect of the particle size of coal which is to be extracted has received little notice in studies of the lower-rank coals. Pertierra¹²² reported that, in the extraction of a lignite (Gualdo Catanes) with anthracene oil, grinding the fuel smaller than 200 mesh had little advantage over 60 mesh. However, the experimental conditions were rather rigorous. It was found possible to attain almost complete solution of the lignite in the solvent mentioned at 375° C, which would probably be above the decomposition temperature of the lignite. Hydrogenation of the lignite solution for 2 hours at 200 atmospheres in the presence of a molybdenum oxide catalyst converted all the organic matter to products which were soluble in ethyl ether and chloroform. Part of the charge (11.5 percent) was converted to gas.

Earlier reference has been made to the method of Bone and coworkers. Some further work by these authors^{35, 123} on brown coals and lignites is summarized in Table XVIII. The data are for extractions carried out, as before, on coal ground to pass a 20- and retained on a 40-mesh screen in a pressure extractor¹²³ working on the Soxhlet principle. The extractions were made with benzene in stages, each of five

¹²¹ Jostes, F., and Siebert, K., *Oel, Kohle, Erdoel, Teer*, **14**, 799-802 (1938).

¹²² Pertierra, J. M., *Anales soc. españ. fis. quim.*, **31**, 779-809 (1933); *Chem. Abs.*, **28**, 2873 (1934).

¹²³ Bone, W. A., Pearson, A. R., and Quarendon, R., *Proc. Roy. Soc. (London)*, **105A**, 608-25 (1924).

TABLE XVIII

RESULTS FROM THE PRESSURE SOXHLET EXTRACTION OF BROWN COALS AND LIGNITES^{35, 123}

Coal	Yield of Fractions in Percentage						
	I(a)	I(b)	II	III'	III	IV'	IV
Morwell brown coal		3.5	1.5	1.0		9.0	
Rhenish brown coal (1)	0.7	2.5	0.6	0.4		1.4	
Rhenish brown coal (2)	1.0	2.5	0.8	2.0		3.2	
Saxon brown coal (1)	1.1	4.4	1.8	1.8		2.6	
Saxon brown coal (2)	0.4	3.3	2.3	trace		1.5	
Estevan brown lignite		1.65	0.3	0.3		2.25	
Burmese lignite	0.1	1.6	1.4	3.45	0.15	4.0	0.45
Canadian lignites							
Cardiff	1.5		1.1		0.35		0.15
Rose Deer	2.2		0.7		0.75		0.20
Pembrina	1.5		1.5		0.60		0.30
Harlech	1.3		1.3		1.20		0.50
New Zealand							
Kaitangata (subbituminous)	2.9		1.7		2.4		1.2

to six days' duration, at temperatures of 240, 260, and 285° C. The coal was given a preliminary atmospheric benzene extraction to remove montan wax. Yields are based on the dry, ash-free coal. The general properties of the fractions were given by Bone and Himus¹²⁴ as:

I. A yellowish-brown, viscous, and usually non-nitrogenous neutral oil of vaseline-like consistency, with a carbon-to-hydrogen ratio less than 10 and low oxygen content. It is soluble in petroleum ether and has an aliphatic constitution. It may be further resolved by steam distillation into (a) and (b) subfractions, the former being volatile and the other not. The I(b) portion may be regarded as containing the true neutral oils of the original coal.

II. A reddish-brown solid with softening point below 60° C and a carbon-to-hydrogen ratio of about 13. It is soluble in a mixture of 4 parts petroleum ether and 1 part benzene, but insoluble in 10 percent sodium carbonate or sodium hydroxide solution. Its chemical character is not so well defined as that of the other fractions.

III. A non-nitrogenous, reddish-brown, brittle, resinous solid softening usually below 150° C and with a carbon-to-hydrogen ratio of about 12.5 and higher oxygen content than I from the same coal. It is insoluble in a mixture of 10 parts of petroleum ether with 1 part benzene, but soluble in ethyl alcohol and in 10 percent sodium hydroxide but not sodium carbonate solution.

IV. A neutral, amorphous, cinnamon-brown, nitrogenous powder, softening only at temperatures above 150° C (usually between 150 and 250° C) and undoubtedly of a benzenoid nature, its carbon-to-hydrogen ratio being about 15.0. It is insoluble in both petroleum ether and ethyl alcohol, and in 10 percent sodium hydroxide solution.

Bone and Himus stated that it was not possible to lay down any hard and fast rules concerning the composition of the various fractions. However, the oxygen contents of corresponding fractions tended to increase with those of the coals from which they were derived. With a given coal the oxygen content of fraction I was the lowest and that of fraction III usually the highest of the four fractions. Fractions I and III were usually, though not invariably, free from sulfur. Fraction I,

¹²⁴ Bone, W. A., and Himus, G. W., *Coal, Its Constitution and Uses*, Longmans, Green, and Co., London, New York, Toronto, 1936, 631 pp.

from only 1 coal, and fraction III, from only 8 coals, of 31 coals extracted in the Imperial College Laboratories, contained some nitrogen. Fraction IV almost invariably contained substantial amounts of both nitrogen and sulfur. Indeed, the evidence as a whole showed that each of fractions I, III, and IV was substantially homogeneous in the sense of being mainly composed of bodies of similar chemical type. The homogeneity of fraction II was questioned.

Extraction of earthy brown coals of the Morwell type (Morwell deposit in Victoria, Australia) yielded fractions I and II which resembled corresponding bituminous-coal fractions but fractions III and IV were missing, their place being taken by neutral phenolic esters (III') and acidic phenolic bodies (IV'). The special fractionation carried out for these lower-rank coals consisted in successively extracting the benzene solution of extract with (a) 10 percent hydrochloric acid to remove any small quantity of organic bases, and (b) a series of three 10 percent aqueous alkaline (sodium bicarbonate, carbonate, and hydroxide) solutions, after which the remaining neutral bodies were resolved into fractions I and II in the usual way. During the extraction of the benzene solution with alkali a small amount of tarlike material was likely to precipitate. There was some evidence, though not conclusive, that these "tarry" bodies were formed by polymerization, in the alkaline solution, of the phenolic material (IV').

The alkali-soluble fraction of the brown-coal extracts was about 60 percent phenol and 25 percent *p*-cresol together with a small amount of catechol and other higher phenolic materials. A very small amount of basic material soluble in dilute hydrochloric acid was found. After removal of the foregoing materials the remaining neu-

tral material was separated into fractions, two of which, as already noted, resembled fractions I and II of bituminous coal. A third fraction was composed of saponifiable phenolic esters (III'). Fraction I(a) contained hydrocarbons from which, in Morwell brown coal, it was possible to isolate small amounts of diphenyl and mesitylene.

No evidence was found that the phenolic bodies were present in brown coals in the free state; on the contrary, it was suspected that they were "present in some loose molecular association with the main coal substance." On the other hand, there was much presumptive evidence for the view that the origin of the fractions III and IV of subbituminous and bituminous coals lay in the phenolic material of III' and IV'. Bone believed that fractions III and IV were responsible for the coking properties in bituminous coals.

If the maturing of coals involves the production of fractions III and IV from III' and IV', then one would expect that an "intermediate" type of coal would exist in which these four fractions would coexist. Such a situation was found in a black, non-laminated lignite from Nam Ma, Shan States, Burma. The amounts of the various fractions are given in Table XVIII. The Canadian lignites examined contained no phenolic material, nor was there any evidence of loss of gas or water during the extraction period as there was for the brown coals.

Oxidation of the residues of Morwell brown coal, Estevan brown lignite, and a Durham coking coal, "Busty,"^{125, 126} with alkaline permanganate yielded, in addition to carbon dioxide, acetic acid, oxalic acid,

¹²⁵ Bone, W. A., and Quarendon, R., *Proc. Roy. Soc. (London)*, **A110**, 537-42 (1926). Bone, W. A., *J. Roy. Soc. Arts*, **79**, 77-95 (1930); *J. Soc. Chem. Ind.*, **50**, 407-16 (1931).

¹²⁶ See p. 181 of ref. 124.

and succinic acid, most of the benzene-carboxylic acids from phthalic acid to melitic acid (see Chapter 9).

The residue obtained in the benzene pressure extraction of a coal always had a higher carbon-to-hydrogen ratio than the original coal, and moreover this ratio was strongly suggestive of benzenoid structure. Data published by Bone are given in Table XIX. The average ratio for these

TABLE XIX

CARBON-TO-HYDROGEN RATIOS FOR VARIOUS
COALS AND COAL RESIDUES ¹²⁸

Coal	Carbon-to-Hydrogen Ratio	
	Original Coal	Residue
Irish peat	10.8	17.2
Morwell brown coal	13-15	19.2
Rhenish brown coal	14.0	16.7
	13.7	18.2
Saxon brown coal	13.0	17.0
	12.8	15.7
Estevan brown lignite	15.7	19.6
Alberta Bloch lignite	17.3	20.3
S. African (Witbank)		
bituminous	18.2	22.2
Dalton Main bright	15.5	16.7
Dalton Main dull	16.6	17.6
Durham "Busty"	17.5	19.5

coals corresponds to a structure containing on the average less hydrogen than benzene (for which the carbon-to-hydrogen ratio is 12.0) and corresponds to the empirical formula C_6H_4 .

Relatively little other work has been done on the nature of the residue from extractions. Stadnikoff ¹²⁷ defined the residue "Restkohle" as coal freed of bitumens A and C and humic acids which, for sapropelic coals, was reported to consist of a mixture of the polymerization products of unsaturated fatty acids, acid anhydrides, and hydroxy acid lactones. These acids

were aliphatic in nature and contained 10 to 16 carbon atoms.¹²⁸

One of the most useful tools of the organic chemist for separating complicated compounds has been known for more than 30 years yet has been almost completely ignored by coal chemists. The presence of materials unstable toward heat in coal extracts has been repeatedly indicated, yet the brutal tactics of distillation are often relied upon to separate these materials. This thermal instability and the fact that coal extracts are generally fluorescent should suggest a milder form of attack, namely, chromatographic absorption methods. Apparently only two accounts of research along these lines have been published. One of these is due to Zechmeister and Frehden.¹²⁹ In the work of these authors, a light petroleum ether extract of lignite (Várpalota, Hungary) was drawn through a calcium hydroxide column. The bands formed were especially noticeable under a quartz lamp. After the upper half of the column had been eluted with alcohol-light petroleum ether mixtures, the liquid was kept at 0° C. From this solution water-soluble needles or prisms crystallized. This material, a potassium salt, was a powerful reducing agent which apparently belonged to the ascorbic-reducing acid, reductone group. When the filtrate of the above salt was repeatedly chromatographed, a second, well-crystallized but water-insoluble compound was obtained. This material gave the usual sterol reactions and seemed to belong to the triterpene class. It decom-

¹²⁸ Stadnikoff, G., and Wosschinskaja, Z., *Brennstoff-Chem.*, **10**, 81-2 (1929), **11**, 414-6 (1930). Stadnikoff, G., and Weizmann, A., *ibid.*, **10**, 61-3, 401-3 (1929). Stadnikoff, G., *ibid.*, **10**, 417-9 (1929). Stadnikoff, G., *Die Entstehung von Kohle und Erdöl*, F. Enke, Stuttgart, 1930, Chap. IV. Stadnikoff, G., and Egorova, O., *Brennstoff-Chem.*, **17**, 48-9 (1936).

¹²⁹ Zechmeister, L., and Frehden, O., *Nature*, **144**, 331 (1939); *Chem. Abs.*, **33**, 8384 (1939).

¹²⁷ See p. 169 of ref. 3.

posed at 244 to 247° C, was levorotatory, and had a molecular weight close to 400 (in camphor).

In the second paper,¹³⁰ a pyridine extract from coal from the Voroskilov mine in the Donets basin was reported on. The extractions, which were carried out at 180 atmospheres pressure for 6 hours, gave a yield of 30 percent based on the original coal. Solubility of the extract was 10 percent in ethyl alcohol, 30 percent in benzene, and 45 percent in ethyl ether, chloroform, and petroleum ether. Chemical analysis showed 1.13 percent acids and phenols and 4.67 percent bases. The acid and neutral part contained 17 and 22 percent unsaturated compounds, respectively. For the chromatographic analysis, aluminum oxide was used as the adsorbent—a material particularly suited for the adsorption of acidic compounds. No data are available on the success of this work.

Another possibility of separation of the complex mixture of compounds found in coal extracts might lie in the so-called liquid-liquid extraction methods. The difficulty here, probably greater than finding a suitable adsorbent as in chromatographic adsorption work, is to find satisfactory solvent pairs. A few trial runs have been made in the Coal Research Laboratory at the Carnegie Institute of Technology with a small experimental set-up. The solvents tried were phenol and pentane, and the extract used was obtained in the benzene pressure Soxhlet extraction of a Pittsburgh Seam coal. The results were unsatisfactory, apparently as a result of a poor choice of solvents, but the method itself is promising and it is hoped that it may receive further study.

¹³⁰ Urazovskii, S. S., and Rozum, Yu. S., *Ukrain. Khim. Zhur.*, **12**, 525-35 (1937); *Chem. Abs.*, **32**, 4751 (1938).

THE EXTRACTION OF BITUMINOUS COAL

Reference has been made from time to time to the fact that the yield of extract obtained by a given process does not appear to be related to the rank of the coal from which it was obtained. At one point in the coalification process, however, a noticeable change takes place both in the nature and in the amount of the extract. Whereas the lower-rank coals yield, in general, a considerable amount of extract with low-boiling solvents such as benzene, alcohol, ether, and petroleum ether, the yield of extract from bituminous coals with these same solvents is considerably less. This is a general statement, and exceptions will be found. The role played by the waxes and resins, obtainable to a considerable extent in the lower-rank coals, in the transformation to bituminous coals is not clear. There can be little doubt that a marked difference exists in the chemical nature of the extract from these sources. From the bituminous coals, aliphatic compounds isolated are hydrocarbons and not acids, alcohols, esters, carbohydrates, etc., as from peat, brown coal, and lignite. Potonié¹³¹ explained the difference in these bitumens as resulting from a difference in the flora from which each was formed. The possibility exists, too, that such changes in the nature of the extracts may be the result of bacterial action governed by base-exchange mechanisms such as postulated by Taylor.¹³² Other authors¹³³ have pointed out the possibility of hydrocarbon formation by: (1) the hydrolysis

¹³¹ Potonié, H., *Die Entstehung der Steinkohle und der Kaustobiolithen überhaupt*, Gebrüder Bornträger, Berlin, 1910, 225 pp.

¹³² Taylor, E. McK., *Fuel*, **5**, 195-202 (1926), **6**, 359-67 (1927), **7**, 66-71, 127-8, 129-30, 130-4, 227-8, 228-9, 230-8 (1928); *J. Inst. Petroleum Tech.*, **15**, 372-84 (1929).

¹³³ Winter, H., *Glückauf*, **65**, 1405-9 (1929); see also p. 171 of ref. 8.

of waxes; (2) splitting of carbon dioxide from the resulting acids; (3) splitting out of methane to yield unsaturated hydrocarbons; and (4) the polymerization of these unsaturated products to yield cyclic compounds. Though all these steps can be carried out in the laboratory, the temperatures necessary (particularly for the elimination of methane) are higher than those reached in the coalification process. However, it should only be necessary to point out that at lower temperatures a longer time would be required than is permissible in laboratory experiments. Marcussen¹³⁴ has suggested that bituminous coals consist of two forms of polymerized material, one resulting from the resins, fats, and waxes, and the other formed from the original cellulose. The products were thought to be asphalt-like materials and furane derivatives. This concept leaves no room for the fairly well-proved theory that the larger part of the coal mass is benzenoid in structure.

Lack of comparable data renders difficult the task of showing a transition between lignites and bituminous coals. The presence of phenolic material in the presence of fractions III and IV as shown by Bone et al. may indicate such a transformation. Similar findings in the coals of the Collie Field of western Australia have been reported by Kent.¹³⁵ Three of the coals studied, Cooperative, Proprietary, and Stockton, were classed as subbituminous, and two others, Griffin and Cardiff, were subbituminous coals approaching lignites in composition. These coals were lower in hydrogen than would be expected from

their classification. Two samples of the Griffin coal were studied, the second of which was thought to be most representative of the seam.

Extractions of the six coals were carried out in Soxhlets at atmospheric pressure on dry, 100-mesh samples first with benzene and then with ethanol-benzene. The average extraction time with benzene was 40 hours, and the average subsequent extraction time with ethanol-benzene was 60 hours. The yields of extract obtained calculated on a dry, ash-free basis are given in Table XX.

TABLE XX
PERCENT YIELD OF EXTRACT IN SOXHLET EXTRACTION¹³⁵

	Coal					
	Cooper- ative	Pro- prietary	Stock- ton	Griffin No. 1	Griffin No. 2	Cardiff
Benzene-soluble	0.2	0.2	0.1	0.8	0.5	0.5
Alcohol-benzene- soluble	1.0	1.2	0.9	2.6	1.7	1.9
Totals	1.2	1.4	1.0	3.4	2.2	2.4

Further extractions were made on Proprietary, Griffin No. 2, and Cardiff coals ground to 20–40 mesh with ethanol-benzene for 100 hours. The yields were 1.46, 2.40, and 2.67 percent, respectively. The dried extract was then fractionated with alcohol-benzene, petroleum (60 to 80° C), and hot and cold benzene, yielding the following materials:

A. Insoluble in the petroleum fraction but soluble in alcohol-benzene: dark brown to black, brittle, resinlike material.

B. Soluble in hot petroleum ether but insoluble in cold benzene: practically white powder which melted to form a hard, brown, brittle wax. This fraction was missing in the Proprietary coal.

C. Soluble in petroleum ether and cold benzene: soft, dark brown substance of vaselinelike consistency with a dull appearance.

¹³⁴ Marcussen, J., *Chem.-Ztg.*, **42**, 437–9 (1918), **44**, 43–4 (1920); *Z. angew. Chem.*, **31**, 237–8 (1918).

¹³⁵ Kent, C. R., *Proc. Roy. Soc. (London)*, **A163**, 568–74 (1937); *Australian Chem. Inst. J. & Proc.*, **6**, 127–38, 162–9, 207–23 (1939); *Chem. Abs.*, **33**, 6557, 7989 (1939).

The extract from the Proprietary coal was a somewhat harder, clear brown substance. Material similar to extract C was obtained by Himus¹³⁶ in the atmospheric extraction of black lignites, who also showed that it could be further subdivided into: (1) a substance resembling montan wax; (2) steam-volatile oils similar to Bone's fraction I(a); and (3) residual vaselinelike bodies.

Pressure extractions were made on the residue of Griffin No. 2 coal after atmospheric ethanol-benzene extraction, by the method of Bone et al.¹³⁷ The separation scheme was that used for the higher-rank coals. During the separation of fractions I(a) from I(b) and II by steam distillation, a small quantity (0.04 percent) of water-soluble phenolic bodies was isolated. Fractions I(a) and III were found to be partially soluble in 10 percent potassium hydroxide solution; fractions I(b) and II showed a very slight solubility. Fraction IV was insoluble. Similar evidence of acidic properties in those fractions was reported by Himus¹³⁶ in his examination of extracts obtained from black lignites.

In Bone's procedure for the fractionation of the benzene pressure extract of lower-rank coals, the phenolic and acidic bodies were removed before separation into fractions I and II. It seems strange that this procedure was not followed here. The phenolic and acidic materials indicated would have constituted fractions III' and IV' of Bone, and, hence, since III and IV were reported present, this coal would fit in as an "intermediate" (Bone) type of coal. However, the amounts of fraction III and IV reported by Kent are much

smaller than the corresponding material from Burmese lignite. The amounts of fractions I(a), I(b), II, III, and IV found were 0.84, 1.53, 1.69, 2.48, and 0.96 percent, respectively.

On the basis of the description of the products and their analysis, a few general trends were noticeable with rank. The atmospheric-benzene-extract of the Proprietary coal contained no montan wax (extract B); while the resinlike extract A and the soft, cold-benzene-soluble extract C had a higher carbon-to-hydrogen ratio than corresponding materials from the Griffin 1 and 2 and Cardiff coals. Moreover, extract C from the Proprietary coal was distinctly different in appearance from the Griffin and Cardiff coals. Corresponding extract fractions from the Griffin and Cardiff coals were similar in appearance, analysis, and carbon-to-hydrogen ratio. The presence of montan wax in the extracts of Griffin and Cardiff coals is typical of lignite extracts, although the amounts found were small, which was consistent with their semilignitic nature. Griffin No. 1 gave a greater yield than No. 2, which was believed to be due to a greater spore content of the No. 1.

The results of benzene pressure extraction of the Griffin No. 2 coal were in agreement with the results of Bone, Horton, and Tei³⁵ obtained in the extraction of Canadian lignites. Although the yields differed, the extracts were similar in chemical composition and analysis. The Canadian lignites were also low in hydrogen content. According to the findings of Bone, in subbituminous coals the yields of fractions III and IV increase, that of fraction III reaching a maximum and being largely in excess of IV; and at about this same stage both these fractions begin to show evidence of agglutinating power. As the true bituminous coals are approached, fraction IV in-

¹³⁶ Himus, G. W., Ph.D. thesis, University of London, 1933.

¹³⁷ This work was carried out at the Fuel Technology Laboratories of the Imperial College of Science and Technology, London, under the direction of W. A. Bone.

creases, apparently at the expense of III, until, as in the strongly coking coals, IV reaches its maximum both in quantity and agglutinating power, while III decreases to almost zero. Because, as Kent stated, the yield of III from Griffin No. 2 coal was the largest yet obtained of this fraction and the ratio III/IV one of the highest, the coal is indicated to be in a transition state between a true lignite and a subbituminous coal—a classification in agreement with its ultimate analysis. This fact is further indicated by the moderate agglutinating powers found to be associated with III and IV when carbonized with powdered coke. The partial development of phenolic properties in I(a) and the separation of a small quantity of phenols were also stated to be evidence of immaturity. The possibility of these phenols arising from intramolecular changes in alcohols¹³⁸ was, however, considered.

A great part of the literature of solvent extraction resembles alchemy more than science, perhaps as a result of the complex nature of the problem. Failure to recognize the complexity of coal and maintain constant some of the variables of extraction has caused a great deal of confusion. Standardized experimental procedures like those used by Bone and others are of considerable value, since they show similar trends in the nature of the extract of various coals even though the amounts may differ. Only in respect to the bituminous coals has any great effort been made to study the factors involved in the extraction of coal.

The effect of the particle size of the coal to be extracted on yield should be of interest, yet little work was done on this aspect

¹³⁸ Pictet, A. [*Ann. chim.*, (9), **10**, 249-330 (1918)], reported that hydroaromatic alcohols isolated by him in the vacuum distillation of coal were unstable and became partially phenolic in properties.

of the problem until after 1930. The available data would indicate that size does not greatly influence yield until the diameter of the particles approaches 0.001 millimeter, at which point there is a relatively great increase in yield over that for the larger sizes. (Data are available for particles up to about 6 millimeters in diameter.)

Along with the material on particle size some information is available on the effect of time of extraction on yield. The extraction curve for bituminous coal, just like that for brown coal, is not parabolic except possibly during the first part of the process. A few authors have noted that complete solution of the organic material of the coal would not be possible if the extraction time were indefinitely prolonged, and several good methods have been developed for calculating the ultimate yield at infinite time. This figure is unquestionably more significant than a value of yield after some arbitrarily chosen time.

One of the first papers to consider the effect of the size of the coal on yield was due to Fischer, Peters, and Cremer,^{139, 140} who described work on the atmospheric extraction of coal of various particle sizes obtained by grinding the coal in a ball mill. For this study coal from the Mathias Stinnes Mining Company, Seam 16, was used. The choice was fortunate because other data are available for this coal.¹⁴¹ The yield of extract obtained with trichloroethylene after various lengths of grinding time is given in Table XXI.

¹³⁹ Fischer, F., Peters, K., and Cremer, W., *Brennstoff-Chem.*, **13**, 364-70 (1932).

¹⁴⁰ Hankiss, S., and Péter, I., *Szénkísérleti Közlemények*, **2**, 45-57 (1927), had earlier stated that the efficient extraction of coal was attained only if the particle size was not greater than 100-1,000 mesh.

¹⁴¹ Broche, H., and Schmitz, H., *Brennstoff-Chem.*, **13**, 81-5 (1932); *Fuel*, **12**, 47-51 (1933). Broche, H., and Nedelmann, H., *Glückauf*, **68**, 769-79 (1932).

TABLE XXI

EFFECT OF GRINDING TIME ON YIELD OF EXTRACT¹³⁹

Grinding Time hours	Yield of Extract After 20 Hours' Extraction percent
1	1.8
4	4.5
4	4.6
4	4.7
8	6.4
16	9.5

Increases in grinding time beyond 16 hours did not increase the yield. A microscopic examination of the ground coal showed that after 16 hours of grinding the largest particle size was 0.001 mm (μ -coal) and after only $\frac{1}{2}$ hour the particles were found to be smaller than 60 μ . The increased yield from 1.8 to 9.5 percent is, therefore, related to the increase in the μ -size coal but does not, however, seem to be related directly to particle size, as shown in Table XXII. It was pointed out that the grinding gives the best results only when it is carried out in a good vacuum (1 to 3 millimeters of mercury). The explanation for this was thought to lie in a lack of cushioning effect of the gas since coal ground in an atmosphere of inert gas did not give as great a yield of extract. The bright coal was considered separately since it was thought that the constituents of the banded coal might concentrate in the finer sizes. The difference in yield here is not striking. From these data it can be seen that decreased particle size increased the yield but little until the μ -size coal was reached.

Inspection of the data shows that the increase in surface of the particle (calculated on the basis of a cubical particle) is not directly related to yield. To explain the

above results the authors advanced a theory of cell-like structure for the coal which results from the cell structure of the original coal-forming plants, so that in breaking the cell wall by grinding the soluble bitumens are liberated. An analogous behavior to the mechanism assumed here is found in the extraction of resin materials, e.g., lycopodium, from which the oils can be extracted only after destruction of the spore skins.¹⁴²

Against a cell theory of coal extraction the authors pointed out that such a structure cannot be established microscopically and many coals appear as though they were once a gellike mass. However, such things as optical anisotropism¹⁴³ and the isolation of membranous substances from coal¹⁴⁴ were thought to be evidence in its favor. At any rate, an explanation of the sudden jump in yield can be attained without the assumption of a cell structure.

It was shown earlier by two of these authors¹⁴⁵ that the occluded gases of coal could be completely removed only by grinding the coal to μ -fineness, and hence it was felt if the coal was impervious to gas it would also be so toward larger molecules such as solvent or bitumen. Then it would appear that the bitumen is removable only from an extremely thin surface layer and not from the compact coal substance. The sudden jump in yield between the large and μ -size particle indicates that the extractible surface layer can have a thickness of less than 0.001 millimeter. On the basis of such an assumption an attempt was

¹⁴² Ullmann, F., *Enzyklopädie der technischen Chemie*, Urban & Schwarzenberg, Berlin, 1931, Vol. 7, p. 412.

¹⁴³ Hoffmann, E., and Jenkner, A., *Glückauf*, **68**, 81-8 (1932).

¹⁴⁴ Zetzsche, F., and Källin, O., *Braunkohle*, **31**, 345-51, 363-6 (1932).

¹⁴⁵ Fischer, F., Peters, K., and Warnecke, A., *Brennstoff-Chem.*, **13**, 209-16 (1932).

TABLE XXII

EXTRACTION OF COAL WITH TRICHLOROETHYLENE (20 HOURS) ¹³⁹

Particle Size	Percent Yield of Extract		Surface of Coal square centimeters per gram	Weight of a Surface 0.5 μ Thick in Percent of Coal	Percent Yield of Extract by Theory
	Banded Coal	Vitrain			
milli-					
meters					
6	0.55	0.15	7	0.045	0.005
4	0.39	0.18	11	0.075	0.008
2	0.5	0.26	21	0.15	0.015
1.2	0.37	0.27	36	0.25	0.025
0.6	0.35	0.30	71	0.5	0.05
0.3	0.40	0.37	143	1.0	0.1
0.15	0.35	0.23	286	2.0	0.2
0.075	0.37	0.64	572	4.0	0.4
0.052	0.57	1.23	823	5.7	0.6
0.036	1.30	1.90	1,200	8.1	0.8
μ -coal	9.98	12.1	42,800	100	10

made to calculate the fraction of the coal particle which consisted of a surface layer 0.5 μ thick, and from this to determine a theoretical yield. These values are given in Table XXII. The experimental yield of 10 percent from the banded coal of μ -size was used to evaluate constants in the equation for calculating the other theoretical yields. The difference between the calculated and experimentally obtained yield was partially explained away by saying that it was brought about by soluble inclusions in the coal which would be extracted independently of the particle size. This, however, is completely in opposition to earlier statements with reference to the

impervious nature of the coal toward solvents and bitumens.

The results from the atmospheric extraction of μ -coal with various solvents are given in Table XXIII, and those from the petrographic constituents of this coal ground to μ -size, in Table XXIV. They indicate that the yields from the petrographic constituents decrease in the order vitrain, durain, and fusain.

An anthracite (Sophia-Jacoba Seam), after 16 hours' grinding, yielded only 0.7 percent extract with trichloroethylene. From a low-volatile coal (Langenbrahm Seam), 1.2 percent of extract was obtained, and a high-volatile coal (Brassert) yielded

TABLE XXIII

YIELDS FROM EXTRACTION OF μ -COAL WITH
VARIOUS SOLVENTS¹³⁹

Solvent	Yield percent
Ethanol	1.5
Methanol	2.6
Carbon tetrachloride	5.4
Carbon disulfide	7.5
Dichloroethylene	7.7
Benzene	8.0
Toluene	8.0
Xylene	8.1
Ethanol-benzene (1 : 1)	9.5
Trichloroethylene	10-10.6
Chloroform	10.7
Chlorobenzene	11.6

TABLE XXIV

YIELDS FROM EXTRACTION OF PETROGRAPHIC
CONSTITUENTS OF COAL GROUND TO μ -SIZE¹³⁹

Solvent	Percent Yields of Extract From			
	Banded Coal	Vitrain	Durain	Fusain
1. Trichloroethylene	10.6	12.1	7.5	2.9
2. Benzene	8.1	8.2	4.8	2.5
3. Benzene under pressure	6.9	9.3	8.6	...
4. Carbon disulfide	7.5	9.0	6.3	3.2
5. Benzene after (4)	2.0	0.3	...	1.6
6. Sum of (4) and (5)	9.5	9.3	6.3	4.6

3.6 percent. Two high-volatile coals (Westphalian and Wealdon Seams) gave yields of 4.6 percent.

Further studies have been reported by Asbury¹⁴⁶ on the effect of particle size on the extraction of a Pittsburgh Seam coal,¹⁴⁷ of which the proximate and ultimate analyses were as follows, in percentage: volatile matter 33.6, fixed carbon 57.0, ash 7.5, moisture 1.9, carbon 77.4, hydrogen 5.2, nitrogen 1.6, sulfur 1.0, and oxygen 7.3. Extractions were made in a specially

designed pressure Soxhlet extractor similar in principle to that used by Bone¹²³ and constructed almost entirely of stainless steel. The extractions were made in stages, the first of which were the shortest in order to minimize risk of changes in composition of the extract. The first stages were also made at temperatures slightly lower than subsequent ones. The yield was determined by removing the extract in benzene solution from the bomb and taking three aliquot samples which were extracted at atmospheric pressure to redissolve any precipitated extract and separate the extract from any fine coal which might have been washed from the thimble or wire basket during extraction. The benzene was then removed by evaporation and the yield for the stage calculated on the average of the three samples. The loss of highly volatile materials with the benzene would tend to make the reported yields low. However, the presence of such material has never been indicated in the extract of this coal. Because of difficulty in removing benzene from the residue, Asbury believed that this procedure constituted the most satisfactory method of determining the yield. Material balances which were made on all runs were usually within 2 percent of 100. In run 18, however, on the extraction of μ -size coal, a balance of 116 percent was obtained. It was reported that retention of benzene by the coal residue was responsible for this gain.

Preliminary runs made by Asbury at temperatures between 220 and 260° C with benzene indicated that most of the extract was removed in the first few hours with a somewhat regular decrease in yield with continued time of extraction. Three sizes of coal were considered: 4 to 8, 16 to 20, and 60 to 80 mesh. The yields from these three sizes were approximately the same

¹⁴⁶ Asbury, R. S., *Ind. Eng. Chem.*, **26**, 1301-6 (1934).

¹⁴⁷ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 525* (1932), 60 pp.

TABLE XXII

EXTRACTION OF COAL WITH TRICHLOROETHYLENE (20 HOURS) ¹³⁹

Particle Size	Percent Yield of Extract		Surface of Coal square centimeters per gram	Weight of a Surface 0.5 μ Thick in Percent of Coal	Percent Yield of Extract by Theory
	Banded Coal	Vitrain			
milli-meters					
6	0.55	0.15	7	0.045	0.005
4	0.39	0.18	11	0.075	0.008
2	0.5	0.26	21	0.15	0.015
1.2	0.37	0.27	36	0.25	0.025
0.6	0.35	0.30	71	0.5	0.05
0.3	0.40	0.37	143	1.0	0.1
0.15	0.35	0.23	286	2.0	0.2
0.075	0.37	0.64	572	4.0	0.4
0.052	0.57	1.23	823	5.7	0.6
0.036	1.30	1.90	1,200	8.1	0.8
μ -coal	9.98	12.1	42,800	100	10

made to calculate the fraction of the coal particle which consisted of a surface layer 0.5 μ thick, and from this to determine a theoretical yield. These values are given in Table XXII. The experimental yield of 10 percent from the banded coal of μ -size was used to evaluate constants in the equation for calculating the other theoretical yields. The difference between the calculated and experimentally obtained yield was partially explained away by saying that it was brought about by soluble inclusions in the coal which would be extracted independently of the particle size. This, however, is completely in opposition to earlier statements with reference to the

impervious nature of the coal toward solvents and bitumens.

The results from the atmospheric extraction of μ -coal with various solvents are given in Table XXIII, and those from the petrographic constituents of this coal ground to μ -size, in Table XXIV. They indicate that the yields from the petrographic constituents decrease in the order vitrain, durain, and fusain.

An anthracite (Sophia-Jacoba Seam), after 16 hours' grinding, yielded only 0.7 percent extract with trichloroethylene. From a low-volatile coal (Langenbrahm Seam), 1.2 percent of extract was obtained, and a high-volatile coal (Brassert) yielded

TABLE XXIII

YIELDS FROM EXTRACTION OF μ -COAL WITH
VARIOUS SOLVENTS¹³⁹

Solvent	Yield percent
Ethanol	1.5
Methanol	2.6
Carbon tetrachloride	5.4
Carbon disulfide	7.5
Dichloroethylene	7.7
Benzene	8.0
Toluene	8.0
Xylene	8.1
Ethanol-benzene (1 : 1)	9.5
Trichloroethylene	10-10.6
Chloroform	10.7
Chlorobenzene	11.6

TABLE XXIV

YIELDS FROM EXTRACTION OF PETROGRAPHIC
CONSTITUENTS OF COAL GROUND TO μ -SIZE¹³⁹

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¹⁴⁶ Asbury, R. S., *Ind. Eng. Chem.*, **26**, 1301-6 (1934).

¹⁴⁷ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper* **525** (1932), 60 pp.

after 41 hours of extraction. This was particularly true for the two smaller sizes. Data from four typical runs are given in Table XXV. The yields are reported on a dry, ash-free basis. The noticeable difference between loss of weight of the coal and yield of extract was reported to be due to retention of solvent by the residue.

TABLE XXV

EFFECT OF PARTICLE SIZE ON YIELD OF EXTRACT¹⁴⁸

Coal size, mesh	4-8	4-8	16-20	60-80
Temperature, °C	220	220	220	160
	240	240	240	180
	260	260	260	200
				220
				240
				260
Number of stages of extraction	17	17	16	15
Total time of extraction, hours	47	47	44	41
Coal sample weight in grams (as-received basis)	250	250	250	250
Loss in weight of coal (as-received basis), percent	12.8	11.4	14.0	18.3
Yield of extract at end of run, percent	14.0	14.7	16.3	16.3
Yield of extract at end of run (dry, ash-free coal basis), percent	15.5	16.2	17.8	18.0
Yield at 41 hours, percent	13.6	14.3	16.0	16.3
Yield at 41 hours (dry, ash-free basis), percent	15.0	15.8	17.5	18.0

The duration of the above runs was determined by the time required to yield a practically colorless extract, a criterion which has been used by others. Although this length of time was at first thought to be sufficient, later work showed that even when the solvent siphoning was colorless a small amount of material was still being removed.

It is of interest to note here that data are available on the extraction of Edenborn coal through 4-mesh size with a Fischer-type extraction apparatus¹⁴⁸ fol-

¹⁴⁸ Fischer, F., Broche, H., and Strauch, J., *Brennstoff-Chem.*, **5**, 299-301 (1924), **6**, 33-43 (1925). Fischer, F., *Ind. Eng. Chem.*, **17**, 707-11 (1925).

lowing a standard procedure.¹⁴⁹ The coal was treated in an autoclave at 270° C in 4-hour stages (fresh benzene in each stage) until a stage showed the removal of less than 0.5 percent extract. In this way a yield of 14.3 percent (dry, ash-free basis) was obtained in 20 hours in comparison to the 15.5 to 18.0 percent reported in Table XXV, indicating incomplete extraction. Table XXVI gives comparative data for

TABLE XXVI

YIELD OF EXTRACT FROM 16-20 MESH AND

Run Number	18	19
Coal size	μ	16-20 mesh
Temperature, °C	220	220
	240	240
	260	260
Number of stages	64	87
Total time of extraction, hours	302	609
Coal sample weight (as-received), grams	25.0	25.0
Yield of extract at end of run (as-received), percent	26.1	20.1
Yield of extract at end of run (dry, ash-free), percent	28.7	22.0
Yield of extract at 41 hours (as-received), percent	13.5	14.4
Yield of extract at 41 hours (dry, ash-free), percent	14.9	15.7
Theoretical yield at infinite time (as-received), percent	29.0	21.5
Theoretical yield at infinite time (dry, ash-free), percent	31.9	23.5

the extraction of 16 to 20 mesh and μ -c with benzene. When the yield from each of these runs is plotted against time of extraction, both curves continue to rise, but with gradually decreasing slopes. To esti-

¹⁴⁹ Fieldner, A. C., Davis, J. D., Thiessen, R., Kestner, E. B., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **344** (1931), 103 pp.

mate the expected yield at infinite time the yield was plotted *versus* inverse time. At infinite time of extraction ($1/\text{time} = 0$), the extrapolated lines are far apart, termi-

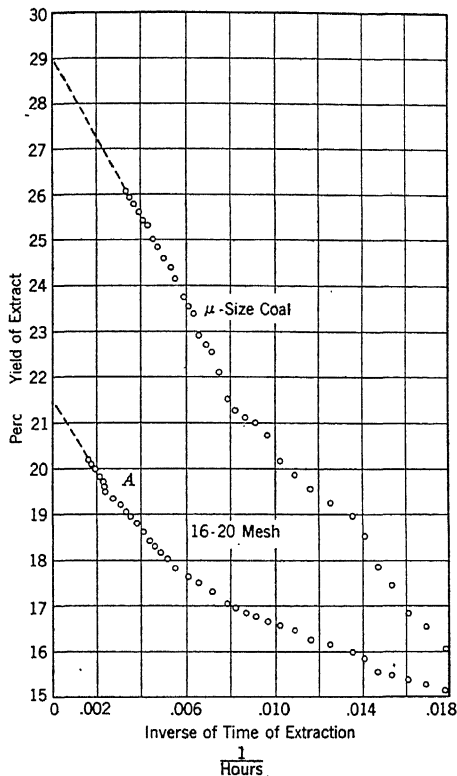


FIG. 3. Yield of extract versus inverse time of extraction for μ size and 16-20 mesh Edenborn coal (as-received basis). At point A the coal residue was ground to pass 200 mesh and the extraction continued.¹⁴⁶

nating at the values given for theoretical yield in Table XXVI.

For comparison, note that 16- to 20-mesh Edenborn coal gives a yield of not more than 0.1 percent of extract in a Soxhlet extraction at 80° C, and 60- to 80-mesh yields only 0.93 percent after 1 hour of extraction at 160° C, whereas at 220° C a half-hour extraction removes 8.9 percent,

again showing the striking effect of temperature.

Figure 3 is a plot of yield of extract against inverse time of extraction. The justification of yields at infinite time estimated by this type of plot lies in the short extrapolation necessary. Later¹⁵⁰ this method was improved somewhat. The method consists in plotting values of time,

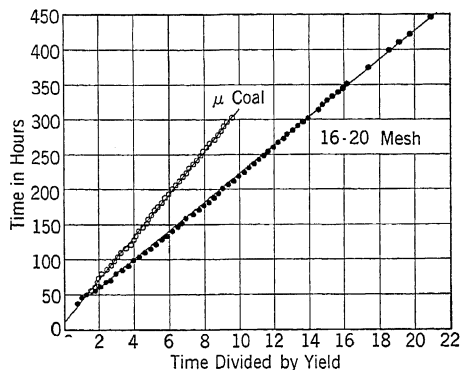


FIG. 4. Time of extraction versus time divided by yield of extract for μ size and 16-20 mesh Edenborn coal.¹⁵⁰

t , against time divided by yield, t/y . When the experimental data are plotted in this way, they lie on a straight line, except for small values of t . If the equation of this line is written as:

$$t = b(t/y) - a$$

where a and b are constants to be determined from the data, then, dividing by t :

$$1 = b/y - a/t$$

and for $t = \infty$, $1 = b/y$; that is, $y = b$. This means that the slope of the line gives the ultimate yield of extract. Figure 4 shows how closely the experimental data for two long runs at 260° C may be fitted to such a line. Only the values of t greater

¹⁵⁰ Landau, H. G., and Asbury, R. S., *Ind. Eng. Chem.*, **30**, 117 (1938).

than 32 hours are plotted. Equations given below were determined for the two runs.

For μ -coal $t = -46.2 + 30.1t/y$
 For 16- to 20-mesh coal $t = -26.0 + 20.6t/y$

The values of ultimate yield obtained in this way are 30.1 percent for μ -coal and 20.6 for 16- to 20-mesh against 29.0 percent and 21.5 percent obtained by the previous method. These differences are not significant, but the later method is superior since it does not require extrapolation beyond experimental data. This method, purely empirical, is justified by the fact that experimental values plotted in this way fall on a straight line except for small values of t as noted. This has been further verified on runs made with aniline and tetralin in the Coal Research Laboratory, on the data of Peters and Cremer,¹¹⁸ using benzene, and on the data of Gryaznov,¹⁵¹ using an alcohol-benzene mixture. It has been reported that the extraction of a series of ten Japanese and Manchurian coals¹⁵² with alcohol-benzene and with benzene followed this rule. In addition the U. S. Bureau of Mines has made use of this method in calculating yield in coal hydrogenation

work. Other data¹⁵³ also tend to indicate that there is an ultimate maximum yield of extract which can be obtained in the extraction of coal with solvents at a given temperature.

A few other authors have studied the effect of particle size on yield. The yield of extract obtained with pyridine has been reported to increase with increasing fineness of the coal,¹⁵⁴ and Agde and Hubertus¹⁵⁵ have reported yields for three types of coal which were ground to μ -size, deashed and extracted with a number of solvents and solvent mixtures.

Peters and Cremer¹¹⁸ have reported data (Table XXVII) from the atmospheric extraction of several coals of various particle size with benzene and acetone for 48 hours. These authors stated that the particle size was almost without influence on the extraction of brown coal; however, the effect on bituminous-coal extraction can be seen in the table. It was also reported that the observed microscopic size of the particle was not a reliable indication of yield

¹⁵³ Oswald, M., and Pinta, R., *Compt. rend.*, **17S**, 1552-5 (1924); *Chimie & industrie*, **12**, 415-22 (1924).

¹⁵⁴ Van Ahlen, A., *Brennstoff-Chem.*, **15**, 401-4 (1934).

¹⁵⁵ Agde, G., and Hubertus, R., *ibid.*, **17**, 149-50 (1936); *Braunkohlenarch.*, No. **46**, 3-30 (1936).

¹⁵¹ Gryaznov, N. S., *Khim. Tverdogo Topliva*, **7**, 222-9 (1936).

¹⁵² Tawada, K., Kawai, N., Takino, F., Ohyama, S., and Kisida, T., *J. Soc. Chem. Ind. Japan*, **12**, Suppl. binding 58 (1939).

TABLE XXVII

YIELD OF EXTRACT AS A FUNCTION OF PARTICLE SIZE¹¹⁸

Particle Size microns	Low-Volatile Coal Ludwig		High-Volatile Coal Stinnes		High-Volatile Coal Lohberg		Cannel Coal Wehhofen		Pittsburgh Seam Coal
	Benzene percent	Acetone percent	Benzene percent	Acetone percent	Benzene percent	Acetone percent	Benzene percent	Acetone percent	
1,200-600	0.06	0.1	0.1	0.3	0.2	1.0	1.1	1.6	0.15
600-300	.1	.1	0.45	0.4	0.25	1.2	1.55	1.8	0.2
300-150	.1	.1	0.17	0.6	0.3	1.4	1.6	2.2	0.4
150-75	.15	.15	0.3	0.6	0.4	2.2	1.9	2.4	0.5
75-52	.16	.3	0.4	0.7	0.5	3.0	2.3	2.7	0.7
52-40			0.5	0.9			2.5	2.9	2.7
40-1	.25	.3	1.35	1.1	0.75	3.9	2.7	2.9	2.7
1 (Average)	.5	.9	9.45	7.8	4.30	10.0	3.7	3.5	13.3

to be expected. In this respect it was found that a coal ground for 8 hours could not be differentiated from one ground for 16 hours, yet it gave only 75 percent as much extract. Peters and Cremer also investigated the effect of time on the extraction of μ -coal (Stinnes?) with benzene in an extractor working on the Soxhlet principle¹⁵⁶ and the solubility of the resulting extracts in pentane. Data from these runs are given in Table XXVIII. When plotted

TABLE XXVIII

YIELD OF EXTRACT AS A FUNCTION OF TIME¹¹⁸

Time of Extraction hours	Ex- tract percent	Soluble in Pentane percent	Differ- ence percent of extract	ΔE $t=K$	
1	1.52	1.15	75.5	0.37	
3	3.08	2.30	74.5	0.78	.34
6	3.91	2.57	65.5	1.34	.28
10	4.63	2.81	60.6	1.82	.18
21	5.28	2.89	54.7	2.29	.06
93	6.34	3.00	47.3	3.34	.015
165	6.94	3.00	43.2	3.94	.008
273	7.40	3.00	40.5	4.40	.006

as in Fig. 5, these data indicate that the extract obtained with benzene consists of two parts, one which is very easily and rap-

¹⁵⁶ Peters, K., *Chem. Fabrik*, **7**, 21-5 (1934).

idly removed, and the second which is much less soluble.¹⁵⁷ The elementary analysis of the pentane-soluble and -insoluble parts does not indicate differences which would satisfactorily explain the differences in properties of these materials which range from oillike materials to difficultly soluble amorphous solids. However, these differences can be explained by the assumption that the extracted material differs chiefly in degree of polymerization rather than in composition. This hypothesis is supported by the fact that coals through hydrogenation¹⁵⁸ can be converted to "pseudobitumens" which have properties similar to the bitumens obtained in extraction with benzene.

The work of Keppeler and Borchers¹¹⁷ on the effect of time and temperature on yield has already been mentioned. These authors extracted finely ground coal (Hamborn-Neumuhl, high volatile) with tetralin at various temperatures (Table XXIX)

¹⁵⁷ Somewhat similar results were obtained by Illingworth, S. R., *Fuel*, **1**, 213-9 (1922), in the extraction of coal with phenol.

¹⁵⁸ Fischer, F., Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 181-4 (1933); *Fuel*, **12**, 390-4 (1933).

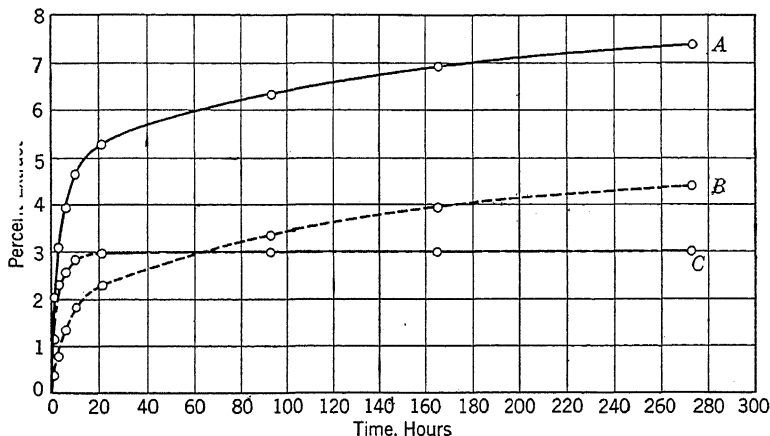


FIG. 5. Effect of extraction time on yield and composition of extract.¹¹⁸ A. Total extract. B. Pentane-insoluble part of extract. C. Pentane-soluble part of extract.

TABLE XXIX

EFFECT OF TEMPERATURE ON YIELD OF EXTRACT¹

Temperature °C	Yield of Extract percent
150	1.4
200	2.5
250	6.2
275	10.4
300	13.3
325	13.5

and at 265° C (100 grams of coal) for increasing lengths of time (Table XXX).

TABLE XXX

YIELD OF EXTRACT FROM SUCCESSIVE 1-HOUR EXTRACTATIONS¹¹⁷

Extraction	Extract grams	Sum of Extracts E grams	$\frac{E^2}{t} =$
1	8.4	8.4	70
2	6.3	14.7	108
3	3.1	17.8	106
4	1.8	19.6	95
5	1.3	20.9	87
6	0.8	21.7	78
7	0.6	22.3	71
Average = 88			

It was found that the above extraction data followed a parabolalike course when plotted against time. The extent of the deviation can be obtained by inspection of the values of c . Calculated values of c for the data of Peters and Cremer show greater deviations. For example, in this work values of c for the first 10 hours of extraction lie fairly close to an average value of 2.54 (maximum deviation +0.62), but starting at the twenty-first hour the values fall off rapidly to a value of 0.20. On the other hand, values of the "extraction constants," K ($K = \frac{dE}{dt} \cdot t$) calculated from the individual runs of Peters and Cre-

mer are in much better agreement among themselves than corresponding values calculated for the data of Keppeler and Borchers.

The work of these investigators is difficult to compare since one group (Keppeler and Borchers) used a bomb type of extraction and the other used a Soxhletlike apparatus. Further, the particle size (μ) studied by Peters and Cremer has been shown to have a great effect on the extraction and might even influence the rate of extraction. Finally, in one group the extractions were carried out for only 7 hours and in the other for 273 hours. Both sets of data show a parabolic tendency in the first few hours of extraction (up to 7 or 10 hours).

Gryaznov¹⁵¹ has shown that the data of Keppeler and Borchers fit best on a parabolic curve in which a value for c of 86.85 (obtained by interpolation rather than arithmetic average) instead of 88 is used. A still better expression was found to be $E_1 = at^b$, where E_1 is the percentage of the extracted bitumen based on the organic matter of the original coal, t is time, and a and b are constants depending on the coal. This equation was shown to apply to extraction independently of experimental conditions. For the work of Keppeler and Borchers the best agreement was obtained when $a = 9.5$ and $b = 0.48$. For the alcohol-benzene extractions made by Gryaznov, $a = 0.414$ and $b = 0.32$. The velocity of extraction of a process already started was found to be inversely proportional to $E^{1-b/b}$ (i.e., $\frac{dE}{dt} = \frac{c}{E^{(1-b)}}$) or directly proportional to E and inversely to t for static conditions $\frac{dE}{dt} = \frac{E}{t}$.

A few investigators, noting the increased yield obtained at higher temperatures, have

studied the effect of preheating the coal in a solvent vapor or inert atmosphere followed by extraction. It will be recalled that data presented earlier, on the effects of preheating on peat, were not conclusive since some peats gave an additional yield after heating, and others did not. More extensive work on bituminous coals has shown that, though preheating will increase the yield of extract, there is a limiting temperature beyond which the yield is actually decreased. This behavior should be related to the Pott-Broche effect, and the limiting temperature would be close to the decomposition temperature of the coal or residue which is being treated.

Harger¹⁵⁹ has shown that the yield of extract obtainable with pyridine could be considerably increased if the residue from the Soxhlet extraction of coal with this solvent was heated to 180° C for 34 hours and then subsequently extracted with pyridine. Fischer and Gröppel¹⁶⁰ increased the yield of extract by heating the coal to 550 to 600° C; however, this temperature is far above the decomposition point of the coal.

Illingworth¹⁵⁷ reported that a bituminous coal studied by him which yielded only 1.02 percent of extract after a 24-hour

extraction with liquid phenol at 184° C became 5.58 percent soluble in this solvent (24 hours at 184° C) after the coal was heated to 400° C out of contact with air. Similar data were given for aniline and pyridine. Unfortunately, these extractions were made at odd temperatures and intervals of time so that the results cannot be placed on a strictly comparative basis. The results are nevertheless striking. This increase in yield upon preheating is additional evidence for the polymeric structure of coal.

Data obtained by Clark and Wheeler¹⁶¹ on the extraction and preheating of two English coals are given in Table XXXI. The extractions were made with cold solvent, before and after preheating at different temperatures. The fact that the increased yield of extract is the result of "primary degradation" of the coal has been indicated¹⁶² by showing that the bitumens of thermally treated coals contain more solid fraction insoluble in petroleum ether.

Asbury¹⁴⁶ also made a study of the effect of pre- and after-heating on extraction. In one run, 16- to 20-mesh coal was subjected to an extraction at 260° C for 41 hours to remove the greater part of the

¹⁶¹ Clark, A. H., and Wheeler, R. V., *J. Chem. Soc.*, **103**, 1704-15 (1913).

¹⁶² Gofman, M. V., Kopeliovich, N. A., and Kagan, E. D., *Khim. Tverdogo Topliva*, **4**, 550-64 (1933); *Chem. Abs.*, **28**, 6273 (1934).

TABLE XXXI

PERCENTAGE YIELD OF EXTRACT FROM PREHEATED BITUMINOUS COALS¹⁶¹

Coal Solvent	Parkgate *		Parkgate †		Barnsley *		Barnsley †	
	Chloro- form	Ben- zene	Chloro- form	Ben- zene	Chloro- form	Ben- zene	Chloro- form	Ben- zene
No preheating	1.45	0.37	1.39	0.50	0.73	0.31	1.15	0.59
Preheated at 200° C	1.01	0.41	1.56	0.73	0.86	0.15	1.45	0.53
Preheated at 250° C	2.75	0.54	2.72	0.71	1.20	0.30	2.37	0.34
Preheated at 350° C	5.88	1.35	4.63	1.61	5.15	0.68	4.44	1.27

* Clarain and vitrain.

† Durain.

soluble material. The residue was then heated in benzene vapor at 325° C for 1 hour. After cooling and removal of gas the residue was again extracted at 260° C for 12 hours in four 3-hour stages. The residue was again heated in benzene vapor for 1 hour at 350° C and then extracted as before at 260° C in four stages of 3 hours each. This process of vapor heating and extraction was repeated at 375°, 400°, 425°, and 450° C. The pressures obtained during these heatings ranged between 1,000 and 1,500 pounds per square inch (70.3 and 105.5 kilograms per square centimeter). Table XXXII and Fig. 6 give the data obtained in this run. It will be noted that, after the initial extraction at 260° C, heat-

ing at each temperature increased the incremental yield of extract up to 375° C, beyond which the increase in yield decreased with increase in temperature of preheating. The final yield, 30.2 percent, was considerably greater than the maximum indicated yield for this particle size at 260° C and only slightly less than the indicated yield for μ -coal.

Gas evolution in this run amounted to less than 2 percent of the weight of the coal, and the gas contained considerable quantities of saturated hydrocarbons and hydrogen. The presence of hydrogen at these low temperatures supports the conclusion that hydrogen is one of the primary products of thermal decomposition of this

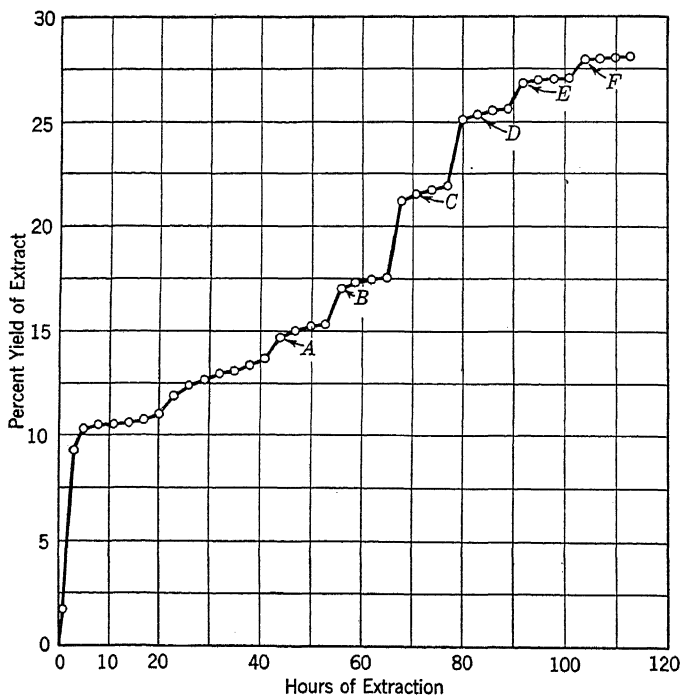


Fig. 6. Yield of extract for coal pre-extracted at 260° C and after-heated at 325 to 450° C.¹⁴⁶

A. First stage after heating at 325° C.
 B. First stage after heating at 350° C.
 C. First stage after heating at 375° C.

D. First stage after heating at 400° C.
 E. First stage after heating at 425° C.
 F. First stage after heating at 450° C.

TABLE XXXII

EFFECT OF AFTERHEATING ON YIELD OF EXTRACT ¹⁴⁶

Temperature of Heating °C	Increase in Yield in Four 3-Hour Stages of Extraction Following Heating *
	percent
325	1.75
350	2.38
375	4.74
400	3.91
425	1.55
450	1.12
	———
	15.45
Amount removed in pre-extraction at 260° C in 41 hours, percent	14.7
Total	30.2

* Dry, ash-free basis.

coal. (See Chapter 20.) In two other experiments the coal was preheated in benzene vapor for 1 hour followed by 31 hours of extraction at 260° C with benzene, then subjected to alternate heating and 12 hours of extraction at 260° C in four 3-hour stages. In the first of these runs the temperature of treatment was 350° C, and in the second, 400° C; the yields were about 22 and 20 percent, respectively. In both runs a small amount of caking was noticed. The curves for both runs are shown in Fig. 7. In another run the coal was preheated at 450° C, but here caking was so severe that extraction was impossible.

From the above data it can be seen that the maximum yield of extract was obtained by removing the extract in steps as the temperature was progressively increased rather than by removing it at one time at the highest temperature studied. For example, the run for which data are shown in Table XXXII gave a yield of 27.48 percent in the extraction following the 400° C

heating (89 hours total extraction time), whereas in the experiment in which the coal was preheated to 400° C before extraction the yield was only around 20 percent (67 hours). The difference in time will hardly explain the difference of more than 7 percent in yield. However, an explanation may be found in the work of Pott, Broche, et al.¹¹⁶ These authors were able to show that as much as 80 percent of extract could be obtained from a bituminous coal and as much as 94 percent from a brown coal of ordinary particle sizes (1 to 2 millimeters) under carefully regulated conditions. Table XXXIII gives data from

TABLE XXXIII

EXTRACTION OF COAL WITH TETRALIN AT 320° C ¹¹⁶

Extraction	Yield percent
1	25.0
2	8.5
3	6.3
4	5.5
5	5.1
6	3.6
7	1.9
8	1.0
9	0.8
Total	57.7

the extraction of a high-volatile coal having a decomposition temperature of 330° C with tetralin. The extractions were carried out at 320° C in nine stages of 2.5 hours each.

These authors did not think that any hydrogenation took place at 320° C from the tetralin since when this solvent was heated in an autoclave at this temperature for several hours no change in composition was noted. It would probably have been better if this test had been conducted in the presence of coal and then hydrogen bal-

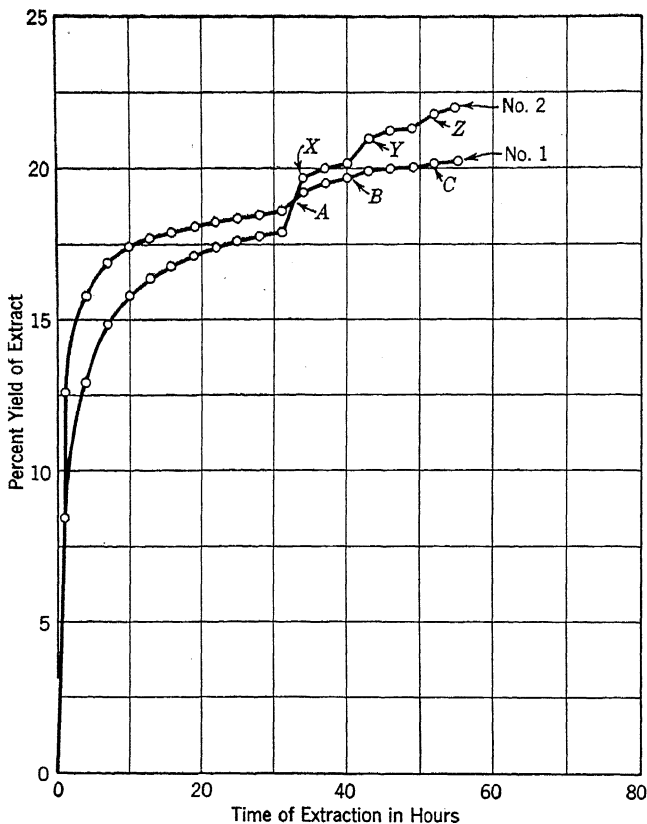


FIG. 7. Effect of preheating at two temperatures followed by extraction and after-heating on yield of extract.¹⁴⁸ Curve 1 at 400° C; curve 2 at 325° C.

A, B, C. First stages after reheating at 400° C.

X, Y, Z. First stages after reheating at 350° C.

ances made on the products. The stability of this solvent appears to be fairly well established at temperatures up to 300° C.^{108, 163, 164, 165} Kiebler has reported that at 300° C hydrogen balances on 120-hour runs with tetralin were over 100 percent. Pott, Broche, et al. reported the decomposition point of tetralin to be in the

neighborhood of 370° C. Asbury pointed out the possibility of formation of tetralin polymers at elevated temperatures which might serve to explain the high hydrogen balances obtained by Kiebler. Péter¹⁶⁶ found that tetralin decomposed to an extent of 33 to 38 percent to naphthalene at 400° to 440° C (1 hour). This is well above the decomposition temperatures of most coals.¹⁶⁷

¹⁶³ Berl, E., and Schildwächter, H., *Brennstoff-Chem.*, **9**, 105-13, 121-2, 159-60 (1928).

¹⁶⁴ Asbury, R. S., *Ind. Eng. Chem.*, **28**, 687-90 (1936).

¹⁶⁵ Kiebler, M. W., *ibid.*, **32**, 1389-94 (1940); *Gas J.*, **232**, 433-6 (1940).

¹⁶⁶ Péter, I., *Technika (Budapest)*, **19**, 193-4 (1938); *Chem. Abs.*, **32**, 6432 (1938).

¹⁶⁷ Holroyd, R., and Wheeler, R. V., *J. Chem. Soc.*, **131**, 3197-203 (1928).

In an investigation of the decomposition temperature of several coals it was found by Pott, Broche, et al. that the residue always had a higher decomposition temperature than the original coal. The decomposition temperature here was defined as that point where a rapid evolution of gas (mostly methane) took place when the coal or residue was heated under special conditions. Table XXXIV gives the results obtained in the extraction of coal at progressively increasing temperature, just under the temperature of decomposition of the coal or residue.

The most important point established in this work was the fact that the temperature of extraction should lie just below the decomposition temperature of the residue in order to produce the greatest yield, and

TABLE XXXIV

SUCCESSIVE EXTRACTIONS OF COAL AND RESIDUE WITH TETRALIN ¹¹⁶

Extraction	Temperature of Extraction °C	Temperature of Decomposition of Material Extracted °C	Yield on Dry, Ash-Free Coal percent
1	320	330	20.3
2	380	380	25.8
3	385-390	395	18.2

Total 64.3

that it is unnecessary, and even detrimental, to exceed this value. It was further shown that after a number of extractions the temperature of decomposition of the residue reached a maximum value which was characteristic for each coal; beyond this point further extraction did not increase the yield. A number of coals were

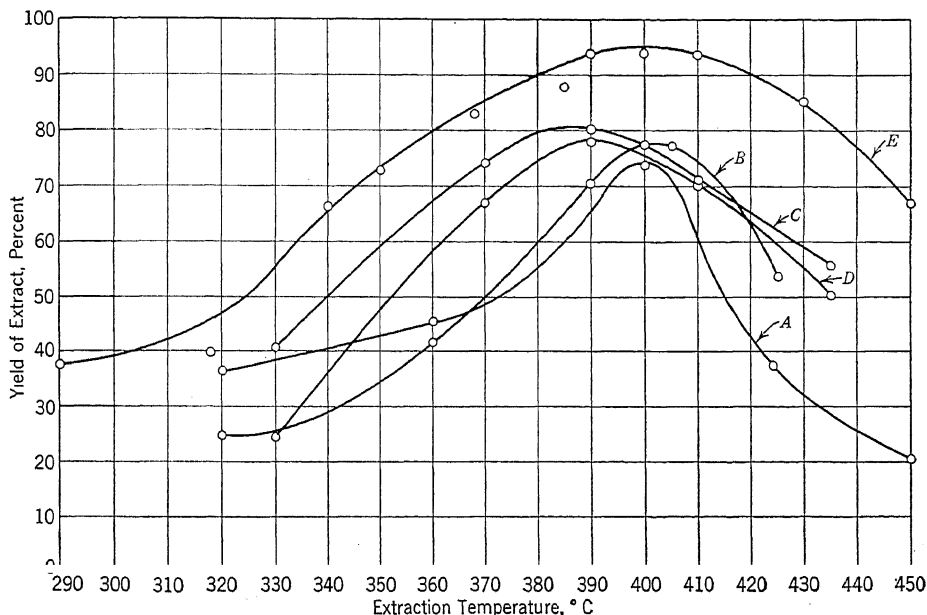


FIG. 8. Influence of extraction temperature on yield of extract with mixture of naphthalene, tetralin, and tar phenols as solvents.¹¹⁶

A. High-volatile coal 1.

B. High-volatile coal 2.

C. High-volatile coal 3.

D. Upper Silesian coal.

E. Brown coal.

extracted at temperatures which were below, coincident with, or above their decomposition temperatures. The results are shown graphically in Fig. 8. The solvents used were either a mixture of 40 percent naphthalene, 40 percent tetralin, and 20 percent low-temperature tar phenols (boiling point 180 to 230°C), or mixture of tetralin and phenols (1 : 1). All the curves show that there is a single optimum temperature of extraction. This point is at the decomposition temperature of the coal.

It was found in this work that, when the extract obtained with phenol alone was mixed with the residue and the mixture was coked, the resulting mixture had lost the coking properties of the original coal. If, on the other hand, a tetralin-phenol mixture was used to extract the coal and the resulting extract and residue were mixed and coked, a well-formed coke button, corresponding to that from the original coal, was formed.

The extracts obtained by the above procedure are easily hydrogenated, yielding a large percentage of benzene-soluble oils. Numerous patents and articles are to be found in the literature on the hydrogenation of coal and coal extracts¹⁶⁸ in the presence of such solvents as tetralin or tetralin-phenol mixtures,¹⁶⁹ phenols and cresols,¹⁷⁰ anthracene,¹⁷¹ phenol,¹⁷² and bi-

phenyl.¹⁷³ This list is not by any means complete. (For further work on hydrogenation in the presence of solvents see Chapter 38.)

One important variable in the extraction of coal remains for consideration, namely, the effect of the nature of the solvent. In spite of the obvious variations in yield of extract found with different solvents, only a few workers have attempted to study this factor of extraction systematically. Extractions which have been reported with solvents of different chemical nature are frequently made at widely varying temperatures, corresponding to their boiling points, so that evaluation of the results is difficult. It can be shown, however, that at constant temperature there is a great difference in the solvent action of aliphatic and nonaliphatic solvents. All available data indicate that the acidic or basic nature of the nonaliphatic solvents is without effect in determining yield. When the physical properties of the solvent are considered it is found that although several would appear to have a theoretical basis for correlation with yield only one such correlation is possible, namely, with internal pressure.

Pew and Withrow¹⁷⁴ carried out atmospheric Soxhlet extractions of an Ohio coal (Pittsburgh No. 8 Seam) with a number of solvents and obtained the data given in Table XXXV. The extractions were carried out to apparent completeness. The effect of oxidation, noted by others, on yield and material balances is well demonstrated by the difference between the runs made in air and in carbon dioxide. The high material balances obtained in some runs may be

¹⁶⁸ I. G. Farbenindustrie A.-G., Ger. Pat. 554,386 (1926). Mohrle, G., *Can. Chem. Met.*, **19**, 96-7 (1935); *Chem. Abs.*, **29**, 4547 (1935).

¹⁶⁹ Pott, A., and Broche, H., U. S. Pat. 1,881,927 (1933), 2,123,380 (1938). Siegmund, E., *Feuerungstech.*, **24**, 158-9 (1936). Levi, M. G., DeBartholomaeis, E., and Magaldi, F., *Studi ric. comb.*, **6**, 259-74 (1936-7); *Chem. Abs.*, **33**, 6024 (1939). Berthelot, C., *Genie civil*, **110**, 266-8 (1937). Gewerkschaft Mathias Stinnes, Fr. Pat. 819,317 (1937). Sander, A., *Teer u. Bitumen*, **36**, 269-71 (1938). Pfärrmann, T. W., U. S. Pat. 2,167,250 (1938). Pott, A., U. S. Pat. 2,141,615 (1938). International Hydrogenation Patents Company, Fr. Pat. 840,763 (1939).

¹⁷⁰ International Hydrogenation Patents Company, Fr. Pat. 831,885 (1938).

¹⁷¹ Beuschlein, W. L., and Wright, C. C., *Ind. Eng. Chem.*, **25**, 409-10 (1933).

¹⁷² Beuschlein, W. L., and Wright, C. C., *ibid.*, **24**, 1010-2 (1932).

¹⁷³ Beuschlein, W. L., Wright, C. C., and Williams, C. M., *ibid.*, **26**, 465-6 (1934).

¹⁷⁴ Pew, J. C., and Withrow, J. R., *Fuel*, **10**, 44-7 (1931).

TABLE XXXV

EXTRACTION OF COAL WITH VARIOUS SOLVENTS ¹⁷⁴

Solvent	Boiling Point of Solvent °C	Hours of Extraction	Residue percent	Extract percent	Total percent
Pyridine *	115	24	70.1	35.0	105.1
Benzene	81	8	98.7	0.6	99.3
Ethylene glycol monoethyl ether	132-35	16	91.8	9.4	101.2
Ethylene glycol monobutyl ether	165-69	24	90.4	12.4	102.8
Ethylene glycol monoethyl ether acetate	147-47	10	98.5	1.8	100.3
Ethylene glycol monomethyl ether	120-23	20	89.2	10.3	99.5
Ethylene glycol diethyl ether	118-22	20	93.5	5.9	99.4
Pine oil	200-210	12	97.4		
Mesityl oxide	125-35	30	85.1	20.1	105.2
Furfural	161	7	82.0	45.6	127.6
Benzaldehyde	176-78	8	75.0	39.8	114.8
Diethylene glycol monoethyl ether	188-92	20	91.0	12.6	103.6
Benzaldehyde *	176-78	8	78.2	33.1	111.3
Ethylene glycol monoethyl ether *	132-35	16	90.0	10.5	100.5
Phenol *	183	16	63.8	43.6	107.0
Phenol	183	16	70.1	43.9	114.0
Ethylene oxide	11		95.2		
Rosin †		2	96.9		
10% NaOH solution ‡		2	97.5		
Ethylene glycol monoethyl ether—KOH ‡		2	70.5	31.3	101.8

* Extracted in atmosphere of carbon dioxide.

† Rosin and coal heated together at 220° C.

‡ Coal and solvent boiled together.

due to oxidation, chemical combination between solvent and coal, mechanically retained solvent, and/or decomposition of the solvent to yield nonvolatile material. The solvents which gave the greatest yield of extract appeared to be most affected by oxidation. In the experiments with phenol as solvent, for example, the weights of extract were approximately the same for the two extractions, indicating that the greater susceptibility to oxidation lies in the residue.¹⁷⁵ Furfural and benzaldehyde probably combined chemically with the coal. It

can be seen that the monoalkyl ethers of ethylene and diethylene glycol dissolved 10 to 12 percent of the coal, the amounts varying only slightly with the boiling point of the solvent. The authors thought that the solvent power appeared to be related to the presence of OH groups, although glycol itself was a very poor solvent for coal. Removing the OH group from a glycol monoalkyl ether by forming the diether reduced the solvency to a considerable extent, and esterification of the OH group with acetic acid almost completely eliminated the solvent power. The residue obtained with potassium hydroxide in ethylene glycol monoethyl ether (normal solubility) showed a very great affinity for

¹⁷⁵ Graham, J. I., and Hill, J., *Trans. Inst. Mining Engrs. (London)*, **54**, 197-224 (1917-18); *Trans. North Engl. Inst. Mining Mech. Engrs.*, **68**, 37 (1918).

oxygen. In one determination this material ignited spontaneously when brought into the air from an oven at 150° C.

Asbury¹⁶⁴ studied the effect of three powerful nonaliphatic solvents—*aniline*, *tetralin*, and *phenol*—on coal. The coal used was the same Pittsburgh Seam coal referred to previously¹⁴⁶ (16–20 mesh), and the apparatus was the same as that previously described except that the water-cooled condenser of the pressure Soxhlet was replaced by an oil-cooled condenser and a device for indicating the frequency of siphoning was built into the extractor.¹⁷⁶ Several slight changes were made in the experimental procedure to conform to the physical and chemical nature of the solvent. Summarized data are given in Table XXXVI. In

TABLE XXXVI

YIELD OF EXTRACT WITH ANILINE, TETRALIN,
AND PHENOL¹⁶⁴

	Solvent	Aniline	Tetralin	Phenol
Time, hours at:	225° C	464		
	250° C		136	44
	300° C		126	21
	350° C		108	
	400° C		4	
	Total	464	374	65
Total number of stages	72	79	23	
Coal sample weight, grams	125	150	150	
Loss in weight of coal, grams	57.3 *	95.5	87.3	
Percent	45.8 *	63.7	58.2	
Weight of extract, grams	53.4 *	117.1	97.5	
Yield of extract, based on original weight of coal, percent	42.7 *	78.1	65.0	
Yield of extract corrected for fine coal, percent	47.0 †	85.5	66.7	
Yield at infinite time, corrected for fine coal, percent	57.0 †	790	68	
Weight of extract plus fine coal plus residue, grams	121.1 *	171.6	160.2	
Balance, percent ‡	96.8 *	114.3	107.0	

* Corrected for aniline assumed to be in products at end of run, based on nitrogen content.

† Estimated.

‡ Equal to $\frac{\text{Extract} + \text{Fine coal} + \text{Residue}}{\text{Original weight of coal}} \times 100$.

176 Asbury, R. S., *Ind. Eng. Chem., Anal. Ed.*, **8**, 152 (1936).

the tetralin runs, the high oxygen content of the end products indicated oxidation of the extraction products and the excess hydrogen content was attributed to the tetralin and its polymers. In agreement with others tetralin was found to decompose around 400° C. Difficulties of a similar nature were encountered with phenol, but at a lower temperature. The decomposition of a very small amount of phenol to diphenyl ether at 300° C was definitely established. Asbury examined the aniline and phenol extracts in their respective solvents with the dark-field microscope at magnifications up to 980 diameters and found numerous colloidal particles below μ -size in Brownian movement, but in the tetralin extract only aggregates of particles not in motion were found. Since these solutions were examined at room temperature, it is probable that the extract was in true solution under the conditions of extraction, in agreement with the studies on benzene pressure extracts which were found to contain very little colloidal material.¹⁴⁶

Kuznetsov¹⁷⁷ extracted Russian coal (Ataman Seam) with a number of solvents, obtaining the data given in Table XXXVII. These extractions were made by boiling 1 gram of the coal with 50 milliliters of solvent for 10 minutes, after which the mixture was allowed to stand above the melting point of the solvent for 36 hours. At the end of this time the mixture was again boiled for 30 minutes, filtered, and the residue washed with low-boiling solvents such as alcohol or ether. In several cases duplicate runs were made which gave some indication of experimental error. The data in Table XXXVII indicate the importance of benzene or pyridine rings in the solvent. The presence of amino and hydroxyl (phe-

177 Kuznetsov, M. I., *Khim. Tverdogo Topliva*, **6**, 515–30 (1935); *Chem. Abs.*, **30**, 3618 (1936); *Fuel*, **16**, 114–21 (1937).

TABLE XXXVII

EXTRACTION OF ATAMAN SEAM COAL ¹⁷⁷

Solvent	Boiling Point °C	Yield of Extract on Basis of Original Coal	
		percent	
Pyridine	118	23.30	22.64
α -Picoline	129	21.74	
Lutidine	155	23.04	20.84
Collidine	180-90	18.34	
Quinaldine	246	25.85	
Quinoline	240	31.62	
Aniline	182	22.87	22.11
Toluidine			
<i>ortho</i>	197	22.92	22.89
<i>meta</i>	197	23.23	23.74
<i>para</i>	198	19.53	22.46
<i>o</i> -Anisidine	226	27.31	
Phenetidine	250	22.57	
Methylaniline	190	26.33	
Dimethylaniline	192	8.79	
Diethylaniline	213	7.14	
Diphenylamine	310	11.56	
Methyldiphenylamine	292	0.0	
Acetamide	222	2.51	
Diethylamine	57	2.95	
Piperidine	106	2.65	
Pyrrole	131	0.0	
Phenol	181	21.55	21.88
Cresol			
<i>ortho</i>	190	19.40	
<i>meta</i>	202	20.25	
<i>para</i>	203	20.55	
Thymol	230	5.13	

nolic) groups appears to be important, but it will be shown later that it is not. The difference in yield obtained with the toluidines was thought to be due to inefficient washing of the residue. An active hydrogen in the solvent might influence the yield as shown by the extractions with methyl- and dimethylaniline. The fact that these extractions were made at different temperatures makes comparison of the results difficult.

Further work by this author on the extractions of another Russian coal (Scher-

binsky) is reported in Table XXXVIII. Extraction of coal with some of the solvent mixtures, particularly with naphthalene-quinoline, by the Pott-Broche process, should give very high yields of extract. No material balances were reported.

TABLE XXXVIII

EXTRACTION OF SCHERBINSKY COAL ¹⁷⁷

Solvent	Extraction Temperature °C	Yield of Extract on Basis of Dry, Ash-Free Coal	
		percent	
Commercial naphthalene	220	53.2	54.4
Commercial tetralin	204	12.9	14.4
Crude anthracene	306	59.8	61.4
Crude phenanthrene		52.4	53.4
Coal oil	154	2.4	4.0
Phenol	181	32.1	32.8
Commercial cresols	176	27.8	28.2
Solid phenolic residues	228	7.8	7.6
Aniline	182	33.6	34.2
Commercial quinoline	238	54.7	54.9
Tetralin-phenol (1 : 1)	182	31.7	34.2
Tetralin-naphthalene (1 : 1)	207	27.3	28.2
Tetralin-naphthalene (2 : 1)	206	22.6	23.2
Naphthalene-phenol (1 : 1)	184	36.8	37.6
Naphthalene-quinoline (1 : 1)	220-40	51.6	54.0
Quinoline-phenol (1 : 1)	194	34.7	36.1

These data have served to indicate the great importance of the nature of the solvent in determining yield. Practically none of the accumulated data, however, offers a satisfactory explanation of the difference in yield obtained with the various solvents. Surface tension of a liquid might serve as a criterion of its effectiveness as a solvent, and several authors have considered it as such. Nellensteyn and Roodenburg ¹⁷⁸ have studied the relation between surface tension, temperature, and solubility of asphaltic bitumens. Kreulen and coworkers ¹⁷⁹ have also considered the surface

¹⁷⁸ Nellensteyn, F. J., and Roodenburg, N. M., *Kolloidchem. Beihefte*, **31**, 434-46 (1930); *Chem. Abs.*, **25**, 408 (1931); *15me Congr. chim. ind. (Bruxelles, September 1935)*, **1936**, 1054-7; *Chem. Abs.*, **30**, 5760 (1936).

¹⁷⁹ Kreulen, D. J. W., *Chem. Weekblad*, **29**, 518-21 (1932), **31**, 104-7, 630-3, 663-6, 758-61

tension of a solvent both as an index of its ability to dissolve part of the coal and as a method of resolving the products of extraction obtained with a single solvent. They have shown that when the yields of extract obtained by various workers are tabulated along with the values of surface tension (at room temperature and the temperature of extraction) of the solvent there is a tendency for solvents of low surface tension to give small yields of extract and those with higher values to give greater yields. Unfortunately the data used were obtained on different coals by various experimental procedures and hence are hardly comparable.

According to these authors the product obtained from the extraction of coal is an organosol, consisting of an oily phase and a dispersed phase (micelle phase) containing protective compounds and nuclei of humic substances. There is an intimate connection between these two phases and it was believed that a quantitative separation could not be made between the two, although attempts were made to do so by reextraction of an extract with solvents of different surface tension. Experimentally it was found that the fractions obtained with solvents of low surface tension (petroleum ether, pentane, etc.) when examined (in solution) with an ultramicroscope were optically clear, whereas those obtained with solvents of higher surface tension were not. The micelles were believed to be devoid of caking properties, but this was masked by the adsorbed oily phase which had caking power. The material obtained with solvents of low surface tension differed from the micelle fraction in that it could not be

converted into humic acids upon oxidation. It seems, however, that little can be explained by such a theory which cannot be covered by assuming that the material extracted from the larger part of bituminous coal (with the exception of a very small amount of occluded hydrocarbons) differs chiefly in degree of polymerization or molecular complexity.

Several authors¹⁸⁰ have reported that the swelling or solution of high-molecular-weight polymers, such as cellulose esters and ethers, polystyrol, polyvinyl chloride, rubber, and Bakelite, appears to be related to the function μ^2/ϵ (μ = dipole moment, ϵ = dielectric constant) of the solvent. Ostwald reported that, when surface tensions of 64 solvents were plotted as ordinates against the μ^2/ϵ values as abscissas, liquids having a solvent action for cellulose acetate fell within a small, definitely circumscribed zone. The same was true in a general way for other polymeric materials. Frequently the zone of great solvent activity was surrounded by a bounding region of lower solvent activity, which was in turn surrounded by an unlimited field of swelling or entirely inactive solvents. Agde and Hubertus¹⁵⁵ have reported that the amount of swelling in solvents, and solvation of coal, are related to this function and that the greatest swelling and solvation was found with solvents having dipole moments of about 2.5 and dielectric constants of 13 to 20. The data which they give are too meager, however, to support such a claim.

Kiebler¹⁶⁵ has studied the relation between the physical and chemical nature of solvents and the yield of extract. Extractions were made at 150, 200, 250, and

(1934). Kreulen, D. J. W., and den Otter, H. P., *ibid.*, **31**, 761-5 (1934). Kreulen, D. J. W., *Brennstoff-Chem.*, **16**, 165-9 (1935). Kreulen, D. J. W., and Roodenburg, N. M., *ibid.*, **16**, 365-8 (1935). Kreulen, D. J. W., *Natuurw. Tijdschr.*, **7**, 279-83 (1939).

¹⁸⁰ Ostwald, W., and Ortlow, H., *Kolloid-Z.*, **59**, 25-32 (1932). Ostwald, W., *J. Oil Colour Chem. Assoc.*, **22**, 31-46 (1939). Moll, W. L. H., *Kolloid-Z.*, **85**, 335-41 (1938); *Kolloidchem. Beihfte*, **49**, 1-74 (1939).

300° C in small steel bombs charged with 5 grams of coal and 100 cubic centimeters of solvent for 120 hours, after which the extract and residue were separated by filtration and the residue freed of original solvent and extract in a 120-hour Soxhlet extraction with ethanol-benzene. It might have been better to make the original pressure extractions in a Soxhlet, but the large number of solvents studied would have required a much greater period of time. Moreover, some of the solvents studied had boiling points above the temperature of extraction. It was well established that, under the conditions of extraction, at no time was the solvent saturated with extract.

A statistical analysis was made of the values of yield of extract and various physical properties of the solvent. Among the properties considered were: internal pressure, surface tension at room temperature and that extrapolated to the temperature of extraction, dipole moment, dielectric constant, latent heat of vaporization at the boiling point and at the temperature of extraction, refractive index, specific refraction, molecular volume, parachor, and the ratio of the square of the dipole moment to dielectric constant. Of this group internal pressure gave the most significant relationship to yield, as shown by correlation coefficients.

Internal pressures were calculated by the formula:

$$\text{Internal pressure} = \frac{(\Delta H_v - RT)D}{m}$$

$$= \frac{\Delta E}{V} = P_i$$

where m is the molecular weight of the solvent, D is the density, R is the gas constant in calories per degree, ΔH_v is the heat of vaporization in calories per mole, V is the molecular volume (m/D), and ΔE is the energy of vaporization per mole.

Values of yield and internal pressure are given in Table XXXIX. The solvents studied at 300° C were those of the 200° C list which were proved to be stable at this higher temperature in the presence of coal. The solvents studied at 150 and 250° C were selected from a 200° C plot of yield *versus* internal pressure, in order that data at four temperatures could be placed on a comparative basis.

TABLE XXXIX

YIELD OF EXTRACT FROM A PITTSBURGH SEAM COAL AT SEVERAL TEMPERATURES TOGETHER WITH CERTAIN PHYSICAL DATA FOR THE SOLVENTS USED¹⁶⁵

Solvent	Yield Based on Recovery of Organic Material	Balance on Re- covery of Organic Material	Internal Pres- sure, P_i calories per cubic centimeter
	percent	percent	
150° C			
Ethyl benzene	4.5	100.5	53.5
<i>p</i> -Cymene	4.6	100.8	50.0
Toluene	5.7	100.0	52.2
Naphthalene	11.5	104.0	74.1
<i>o</i> -Phenyl phenol	16.3	99.4	86.5
Phenol	21.0	105.7	120.0
200° C			
Cetyl alcohol	3.0	99.9	61.7
Cyclohexane	3.2	99.5	27.7
Heptane	4.8	97.6	21.6
Ethyl acetate	7.0	101.1	34.5
Ethylene glycol	7.6	100.2	162.2
Ethyl propionate	7.7	100.7	30.8
<i>n</i> -Propyl acetate	8.1	101.3	32.0
Isopropanol	8.1	101.5	39.6
Ethanol	8.3	100.6	54.4
Dibenzyl	9.1	97.9	62.7
<i>p</i> -Cymene	9.3	101.1	41.2
Benzene	9.7	100.6	35.8
Ethyl benzene	9.9	100.8	41.4
<i>n</i> -Propanol	9.9	102.8	57.2
Toluene	10.1	100.8	39.1
<i>n</i> -Butanol	10.9	101.5	57.9
Methyl ethyl ketone	11.0	102.0	30.2
<i>p</i> -Chlorotoluene *	11.1	102.5	52.4

* Corrected for solvent on the basis of excess Cl; yield = 10.7% ; balance = 97.8%.

TABLE XXXIX—*Continued*

YIELD OF EXTRACT FROM A PITTSBURGH SEAM COAL AT SEVERAL TEMPERATURES TOGETHER WITH CERTAIN PHYSICAL DATA FOR THE SOLVENTS USED ¹⁶⁵

Solvent	Yield Based on Recovery of Organic Material	Balance on Re- covery of Organic Material	Internal Pres- sure, P _i	Solvent	Yield Based on Recovery of Organic Material	Balance on Re- covery of Organic Material	Internal Pres- sure, P _i
	percent	percent	calories per cubic centimeter		percent	percent	calories per cubic centimeter
	200° C						
Bromobenzene †	11.9	105.7	57.5	Naphthalene	17.8	102.7	49.7
Carbitol	12.4	100.8	76.5	<i>o</i> -Phenyl phenol	33.2	110.1	70.4
Cellosolve	12.6	101.3	74.1		300° C		
<i>p</i> -Dichlorobenzene ‡	12.9	100.3	67.5	Toluene	16.0	100.2	8.5
Phenyl ether	13.0	101.4	63.0	<i>p</i> -Cymene	18.0	101.1	24.8
<i>n</i> -Hexanol	13.9	103.5	58.8	Ethyl benzene	20.0	101.8	16.3
Biphenyl	14.0	100.2	69.8	Phenyl ether	24.6	100.3	46.1
Chlorobenzene §	14.2	101.7	59.7	Biphenyl	27.9	99.4	53.2
Anisole	14.9	101.8	52.8	Naphthalene	29.6	102.1	36.8
β -Phenyl ethyl alcohol	15.5	99.8	85.9	Dibenzyl	34.0	100.8	48.7
Naphthalene	15.6	100.3	62.3	Pyridine ††	34.9	104.3	24.1
Tetralin	16.3	102.1	61.4	Phenol	39.7	104.4	71.7
Dioxane	16.6	101.5	51.1	<i>m</i> -Cresol	40.4	111.4	53.8
Phenyl salicylate	16.7	104.1	57.0	Aniline ††	48.4	113.9	47.7
Quinoline	17.4	103.3	72.2	<i>o</i> -Phenyl phenol	49.1	111.2	59.9
Phenyl benzoate	19.4	108.5	71.2				
Pyridine ¶	20.0	103.8	56.9				
Methyl benzoate	20.1	106.4	72.9				
Thymol	20.7	104.5	53.8				
Methyl salicylate	20.8	106.7	94.0				
Guaiacol	21.2	104.4	72.6				
Cyclohexanol	21.7	105.5	72.7				
Acetophenone	24.0	100.9	60.7				
Aniline **	24.4	108.3	77.1				
<i>o</i> -Phenyl phenol	25.0	103.8	78.9				
<i>m</i> -Cresol	31.4	105.8	83.0				
Phenol	32.1	105.8	101.3				
	250° C						
<i>p</i> -Cymene	11.6	102.5	32.6				
Ethyl benzene	11.7	103.1	30.0				
Toluene	12.8	102.2	27.4				

† Corrected for solvent on the basis of excess Br; yield = 9.2%; balance = 97.8%.

‡ Corrected for solvent on the basis of excess Cl; yield = 12.9%; balance = 99.6%.

§ Corrected for solvent on the basis of excess Cl; yield = 14.2%; balance = 100.8%.

|| Corrected for solvent on the basis of excess N; no change.

¶ Corrected for solvent on the basis of excess N; yield = 20.1%; balance = 99.7%.

** Corrected for solvent on the basis of excess N; yield = 24.4%; balance = 90.7%.

†† Corrected for solvent on the basis of excess N; yield = 34.9%; balance = 102.7%.

‡‡ Corrected for solvent on the basis of excess N; yield = 48.4%; balance = 96.5%.

NOTE: These corrected yields and balances were made on the assumption that the halogen or nitrogen was distributed through the extract and residue in direct proportion to the amount of each, and, moreover, in the corrections for the nitrogen-containing solvents, it was assumed that the original nitrogen of the coal was distributed proportionately between the extract and residue.

Some additional solvents—carbon tetrachloride, nitrobenzene, catechol, benzaldehyde, benzoic acid, α -naphthol, carbon disulfide, *p*-chlorophenol, furfuryl alcohol, morpholine, bromoform, thiophene, and ethyl carbonate—not shown in the table, were tested at 200° C. These solvents decomposed or reacted with the coal to such an extent that no true value of yield could be obtained. With furfuryl alcohol, polymerization to a hard black mass, insoluble in all solvents tried, occurred. At 300° C, α -naphthol gave a yield of extract of more than 60 percent, but the solvent was entirely transformed to α -dinaphthylene oxide, the hydrogen liberated probably being responsible for the high yield. It might be

pointed out that the thermal stability of a compound alone may not justify its use as a solvent. Several investigators¹⁸¹ have found that coal is capable of serving as an oxidizing agent. Ashmore and Wheeler reported that, in the extraction of coal at elevated temperatures, benzene may be converted to phenol and acetaldehyde was produced when finely ground lignite was boiled in ethyl alcohol. The formation of phenol in benzene extractions was suggested as an explanation for the large amount of phenol found by Bone in the extract of brown coals. These authors further stated that extraction of coal with mixtures of xylene and amyl alcohol resulted in a partial condensation of these materials, with or without subsequent oxidation, to form products which could be confused with the actual extract.

Table XL gives the values of the correlation coefficients obtained and equations relating internal pressure and yield of extract at the temperatures studied.¹⁶⁵ The

TABLE XL

CORRELATION COEFFICIENTS OF YIELD (Y) BASED ON RECOVERY OF ORGANIC MATERIAL *versus* INTERNAL PRESSURE (P_i) AND EQUATIONS RELATING THOSE QUANTITIES AT THE SEVERAL TEMPERATURES STUDIED¹⁶⁵

Temperature °C	Correlation Coefficient	Equation	Number of Solvents
150	0.98	$Y = -7.36 + 0.247P_i$	6
200	0.98	$Y = -5.44 + 0.369P_i$	6
200	0.98	$Y = -5.44 + 0.369P_i$	6
250	0.97	$Y = -3.06 + 0.487P_i$	5
300	0.91	$Y = 8.67 + 0.552P_i$	6
200	0.74	$Y = -1.55 + 0.274P_i$	44 *
200	0.77	$Y = -2.08 + 0.300P_i$	31 †
300	0.73	$Y = 14.31 + 0.429P_i$	12

* All solvents except glycol.

† Nonaliphatic solvents.

¹⁸¹ Ashmore, J. E., and Wheeler, R. V., *J. Chem. Soc.*, **136**, 1405-8 (1933). Yohe, G. R., and Harman, C. A., *J. Am. Chem. Soc.*, **63**, 555-6, (1941).

equations were fitted to the data by a least-squares method, and it was assumed that the relationship between yield and internal pressure was linear since insufficient data were available to indicate that it should be otherwise. The probability of no relation existing between yield and internal pressure was found to be less than 1 in 100 for the smaller groups of solvents and very much less than this for the 44 solvents studied at 200° C.

Figures 9 and 10 are plots of the data obtained in this work. It will be noticed that

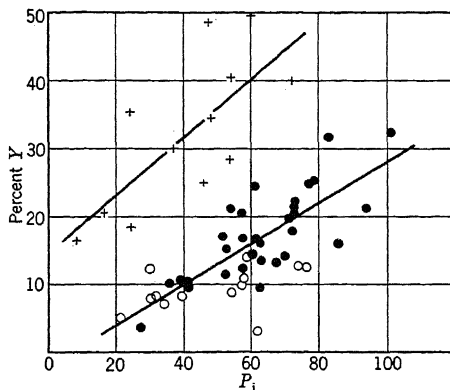


FIG. 9. Yield of extract, Y , based on recovery of organic materials versus internal pressure, P_i , at 200° and 300° C.¹⁶⁵

○ Aliphatic solvents at 200° C.

● Nonaliphatic solvents at 200° C.

+ Nonaliphatic solvents at 300° C.

the lines and equations for the 200 and 300° C data are not the same for the two groups of solvents which were studied at each of these temperatures. These differences are not significant since the probable errors in the constants of the equations are of such magnitude that the differences might be due to chance.

The high values of the correlation coefficients at 150 and 250° C would lose significance because of the small number of solvents studied if it were not for the fact

that good correlations were obtained at 200 and 300° C with larger numbers of solvents. Poorer correlation at 300° C is probably due to two reasons. First, the physical data for the solvents for calculation of internal pressure were extrapolated from known values and hence became more in error as the temperature of extraction departed from the temperatures at which the values were known to be accurate, and sec-

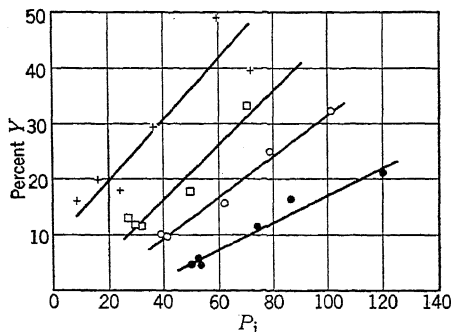


FIG. 10. Yield of extract, Y , based on recovery of organic material versus internal pressure, P_i .¹⁴⁵

● 150° C, ○ 200° C, □ 250° C, + 300° C.

ond, since the experimental error increased with yield, the increase in yield with temperature would be accompanied by an increase in experimental error.

It is surprising that the correlation of yield with internal pressure is as high as observed when it is considered that the solvents studied included such a wide variety of chemical compounds, many of which were strongly polar. Hildebrand¹⁸² considered this function a criterion of solubility for nonpolar liquids only. In determining the coefficients and equations given in Table XL, the data for glycol were not used since they were not concordant with the other data; at 200° C, ethylene glycol

had the highest internal pressure and was one of the poorest solvents studied.

Internal pressure is obviously not the only factor in determining yield. In order to determine whether other factors are independently important, plots were made of the deviations of yield from the line at 200° C against several other physical properties. The scattering of points showed no regular trend in any of the plots, indicating that these properties either have no influence or are automatically taken into consideration in internal pressure—a more likely hypothesis in view of the fact that many physical properties are interrelated. In an attempt to correlate surface tension with yield, it was found that a significant coefficient was obtained at 200° C only with the aliphatic solvents. No significant correlation was obtained at 300° C where only nonaliphatic solvents were studied.

The yield of extract insoluble in a solvent of low internal pressure, such as ethyl ether or pentane, bears a direct relation to the internal pressure of the solvent with which the extract was originally obtained from the coal. If the yield of ether-insoluble material is taken as a measure of the primary degradation of the coal substance, then solvents of high internal pressure not only give greater yields of extract but also do so with less secondary decomposition. When the amount of ether-insoluble material was recalculated on the original coal basis (through the weights of extract found), correlation coefficients with internal pressure very similar to those given in Table XL were obtained.

The equations relating internal pressure and yield are of the form $Y = a + bP_i$ where a and b are constants depending on temperature. The general type of these equations might be interpreted provisionally as supporting the idea that the yield of extract is determined in part by the ex-

¹⁸² Hildebrand, J. H., *Solubility of Non-Electrolytes*, 2nd ed., Reinhold Publishing Corp., New York, 1936, p. 103.

tent of thermal depolymerization of the coal and in part by the extent of solvent depolymerization. Also provisionally, the fact that the value of the constant a becomes positive somewhere between 250 and 300° C may be interpreted to mean that within this temperature range thermal depolymerization has progressed to the stage where the products have a molecular weight of the order of 200 to 500, which is the range observed for extracts obtained with various solvents.

Mathematical analysis of the data given in this paper indicated that on a probability basis the equation for the nonaliphatic solvents was not significantly different from the equation for all the solvents studied (200° C). The equation for the aliphatics, on the other hand, had a much different slope. It was further shown that the difference between nonaliphatics with and without hydroxyl was not significant.

Kuznetsov¹⁷⁷ reported data which indicated that the yield of extract was not governed by the chemical nature of the solvent. When the coal residue from phenol extractions was further extracted with pyridine, the yield was only 1.04 percent. Pyridine alone extracted 22.87 percent (average); phenol, 21.71 percent. The 1.16 percent difference is in good agreement with 1.04 percent when factors such as experimental error and oxidation are considered. Diethylaniline extracted only 7.14 percent, and aniline extracted a further 17.74 percent or a total of 24.88 percent. This figure is only about 2 percent above the figure given for aniline alone. Though agreement closer than this was attained in the two aniline runs, several of the other experiments gave yields which differed by more than 3 percent.

In Kiebler's work, it was reported that when phenol residues were reextracted with aniline, a less powerful solvent, practically

no yield was obtained. On the other hand, if the coal was first extracted with aniline and then with phenol, the total yield obtained was very slightly less than with phenol alone.

These data, and some presented earlier on the extraction of brown coal with benzene and acetone,⁵⁴ might be taken as evidence in support of the theory that the successive extraction of coal with two (or more?) solvents of different solvent power will result in the solution of the same amount of material as would be removed by the better solvent alone. Incomplete extraction in Kuznetsov's work and oxidation between extractions in Kiebler's have introduced errors (apparently, however, within the experimental accuracy of the work) which prevent the absolute establishment of this opinion.

Extraction of coal with phenol has been reported by a number of workers,¹⁸³ Frazer and Hoffmann having made the most elaborate study. By means of this solvent they were able to extract 10.87 percent of a noncoking coal (Franklin County, Ill.) at about 140° C. The extract after being freed of phenol was subdivided by less powerful solvent into various fractions. The many specimens obtained showed varying physical properties and several gave evidence of being pure compounds, but lack of sufficient quantities for study prevented the absolute proof of this opinion. Parr and Hadley extracted two Illinois coals with phenol at

¹⁸³ Guignet, C. E., *Compt. rend.*, **88**, 590-2 (1879). Frazer, J. C. W., and Hoffmann, E. J., *U. S. Bur. Mines, Tech. Paper* **5**, 5-20 (1912). Parr, S. W., and Hadley, H. F., *Illinois Univ. Eng. Exp. Sta., Bull.* **76** (1914), 41 pp.; *J. Soc. Chem. Ind.*, **34**, 213 (1915); *J. Gas Lighting*, **129**, 260 (1915). Gillet, A., and Dettaille, H., *Chimie & Industrie*, **1928**, Spec. No., 164-5. Raaschow, P. E., *Trans. World Power Conf., Tokyo Sect. Meeting*, **1**, 44-71 (1929); *Chem. Abs.*, **26**, 2299 (1932). Suiskov, K. I., and Ushakova, A. A., *Kolloid-Z.*, **76**, 213-6 (1936).

110° C and obtained 35 to 40 percent extract. Both the extract and residue were easily oxidized and readily absorbed moisture and carbon dioxide. It was found that the extract contained more volatile matter than the residue, but both had the same ultimate analysis. Oxidation of the extract and residue lowered the amount of volatile matter from each.

Solvent extraction has played an important part in the study of the chemical constitution of coal. Relative to this, reference has been made to the studies of Bone and coworkers who showed through oxidation of the benzene pressure residues that the greater part of the coal has a benzenoid nature. Other experiments¹⁸⁴ on oxidation of the extract gave similar products. The actual identification of chemical constituents has been frequently reported in the extraction studies of the lower-rank coals but not for bituminous coal. Some work has been reported on the presence of soluble resins^{39, 40, 43, 185} in the higher-rank coals, which have been given names such as middletonite, pyroretine, reussinite, scleretinite, rosthornite, anthrakoxen, guyaquilite, and berengelite.¹⁸⁶ However, their exact chemical nature is not known.

Occluded materials, other than resinous, have been reported from time to time, the origin of which is purely a matter for

speculation. Among the products isolated have been many paraffin hydrocarbons. Compounds such as these could have originated by a decarboxylation of fatty acids as suggested earlier; however, the presence of paraffins in coal seams, usually near a fault,¹⁸⁷ has been reported and perhaps indicates that they were formed at increased temperatures caused by earth movement.

Donath¹⁸⁸ reported that one fraction of an extract obtained from a coking coal (Rossitz) gave color reactions with formaldehyde characteristic of anthracene and chrysene, but neither of these materials could be isolated, and Pictet and Ramsayer¹⁸⁹ succeeded in isolating hexahydrofluorene from the benzene-soluble portion of a high-volatile bituminous coal (Montrambert).

Pictet^{188, 189, 190} and collaborators extracted 5,200 kilograms of a high-volatile Saar coal with benzene at the boiling point, obtaining a yield of 0.25 percent. The part soluble in petroleum ether consisted of a mixture of hydrocarbons, bases, and alcohols, the last two in small amounts. The hydrocarbon mixture was made up of about 25 percent saturated and 75 percent unsaturated compounds. All the saturated hydrocarbons isolated were monocyclic naphthenes. Separation of the extract with acids, bases, solvents (sulfur dioxide and organic), and steam distillation gave the products shown in Table XLI. A few of the fractions had boiling-point ranges

¹⁸⁴ Bone, W. A., Horton, L., and Ward, S. G., *Proc. Roy. Soc. (London)*, **A127**, 480-510 (1930).

¹⁸⁵ Siepmann, P., *Z. Berg-hütten u. Salinenwesen*, **39**, 26-31 (1891). Smith, W., *J. Soc. Chem. Ind.*, **10**, 975-80 (1891). Smith, W., and Chorley, J. C., *ibid.*, **11**, 591-2 (1892), **12**, 221-2 (1893). Wheeler, R. V., and Wigginton, R., *Fuel*, **1**, 10-14 (1922). White, D., *U. S. Geol. Survey, Professional Paper 85*, Part E (1913), p. 66. Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **127**, 2236-45 (1925), **129**, 1410-2 (1926). Hoffmann, E., and Kirchberg, H., *Brennstoff-Chem.*, **11**, 389-94 (1930).

¹⁸⁶ Hinrichsen, F. W., and Taczak, S., *Die Chemie der Kohle*, W. Engelmann, Leipzig, 1916, p. 93. See also p. 203 of ref. 8 and p. 301 of ref. 38.

¹⁸⁷ Kukuk, H., *Glückauf*, **45**, 60 (1909). Cohen, J. B., and Finn, C. P., *J. Soc. Chem. Ind.*, **31**, 12-5 (1912). Stopes, M. C., and Wheeler, R. V., *Fuel*, **3**, 63-7 (1924).

¹⁸⁸ Donath, E., *Chem.-Ztg.*, **32**, 1271-3 (1908).

¹⁸⁹ Pictet, A., and Ramsayer, L., *ibid.*, **35**, 865, 907 (1911); *Ber.*, **44**, 2486-97 (1911).

¹⁹⁰ Pictet, A., Ramsayer, L., and Kaiser, O., *Compt. rend.*, **163**, 358-61 (1916). Pictet, A., and Kaiser, O., *Chem.-Ztg.*, **40**, 211 (1916).

TABLE XLI

COMPOUNDS ISOLATED FROM A BITUMINOUS
COAL EXTRACTION WITH BENZENE 138, 189, 190

Compound	Formula	Saturated
		Boiling Point °C
Naphthene	C ₈ H ₁₆	118-122
Naphthene	C ₉ H ₁₈	135-138
Naphthene	C ₁₀ H ₂₀	172-174
Naphthene	C ₁₁ H ₂₂	190-192
Naphthene	C ₁₂ H ₂₄	215-216
Naphthene	C ₁₃ H ₂₆	227-229
Melene	C ₃₀ H ₆₀	300-302 (0.5 mm)
Unsaturated		
Dihydrotoluene	C ₇ H ₁₀	108-110
Dihydro- <i>m</i> -xylene	C ₈ H ₁₂	135-137
Dihydro-mesitylene	C ₉ H ₁₄	166-168
Dihydro-prehnitene	C ₁₀ H ₁₆	180-182
	C ₁₁ H ₁₆	200-202
	C ₁₁ H ₁₆	214-216
	C ₁₁ H ₁₆	225-227
	C ₁₂ H ₁₆	235-238
	C ₁₂ H ₁₄	264-266
	C ₁₃ H ₁₆	240-250
	C ₁₃ H ₁₆	282-287
	C ₁₃ H ₁₂	251-254
	C ₁₄ H ₁₆	236-238
	C ₁₇ H ₂₀	274-277
	C ₇ H ₁₄ O	170-175
	C ₈ H ₁₀ O	185-190
	C ₉ H ₁₂ O	198-200
	C ₁₀ H ₁₄ O	213-215
	C ₁₁ H ₁₆ O	226-228
Bases		
Toluidine	C ₇ H ₁₃ N	
	C ₇ H ₉ N	198-203
	C ₈ H ₇ N	225
	C ₉ H ₉ N	247-250
	C ₁₀ H ₁₁ N	250-260
	C ₁₁ H ₁₃ N	260-265
	C ₁₂ H ₁₅ N	270-280

which were too wide for pure compounds. The compounds were characterized through their analysis, molecular weight, density, index of refraction, oxidation, reaction with bromine and nitric acid, and through the picrates. The extract was feebly levorotatory ($[\alpha]_D^{20} = -0.08^\circ$), becoming dextrorotatory ($[\alpha]_D^{20} = +0.27^\circ$) after the hydroxy compounds were eliminated. Some of the above compounds were also isolated in vacuum tar and might therefore be regarded as having been derived from the coal by simple volatilization. No optically active compounds were indicated in the tar, and it was suggested that volatile constituents of the coal were racemized at the temperature of distillation (450° C).

Results similar to those of Pictet et al. were obtained by Hofmann and Damm,¹⁹¹ who obtained 51 kilograms of extract by extracting 500 kilograms of an Upper Silesian bituminous coal with pyridine. Of this amount about 15 kilograms was obtained with cold, and the remainder with hot, solvent. This extract was divided into an ether-soluble (22 percent) and -insoluble part, and the soluble was further separated into acidic, basic, and neutral fractions. The neutral ether-soluble part of the extract (16 percent of extract or 1.6 percent of the coal) was subjected to a thorough chemical investigation. Of these neutral oils, about half distilled below 290° C at 1 mm. Separation of this material with solvents and reagents yielded a large number of individual components in an apparently fair state of purity. The formulas assigned to a few of these compounds, however, are questionable. Among the compounds isolated were: (1) solid paraffins, all members from C₂₁H₄₄ to C₂₇H₅₆, inclusive, of which the higher members resembled the "melen" of Pictet, sug-

¹⁹¹ Hofmann, F., and Damm, P., *Brennstoff-Chem.*, **3**, 73-9, 81-91 (1922), **4**, 65-73 (1923). Hofmann, F., *J. Gasbeleucht.*, **64**, 642 (1921).

gesting that melene is actually a mixture of these hydrocarbons;¹⁹² (2) saturated hydrocarbons of the series C_nH_{2n-2} , $C_{11}H_{20}$, $C_{13}H_{24}$ (two compounds with different boiling points), $C_{14}H_{26}$, $C_{15}H_{28}$, and $C_{16}H_{30}$ which boiled from 210 to 295° C; higher-boiling saturated hydrocarbons (b.p. 215 to 270° C at 2 mm), $C_{17}H_{30}$, $C_{17}H_{28}$, $C_{18}H_{28}$ (2 compounds), $C_{19}H_{30}$, $C_{22}H_{36}$ (2 compounds), $C_{32}H_{36}$, and $C_{24}H_{40}$; (3) unsaturated hydrocarbons, C_8H_{12} , C_9H_{14} , $C_{10}H_{16}$, $C_{11}H_{18}$, $C_{12}H_{18}$ (2 compounds), $C_{13}H_{18}$ (3 compounds), $C_{14}H_{18}$ (4 compounds), $C_{15}H_{20}$, $C_{16}H_{20}$ (3 compounds), $C_{17}H_{22}$, $C_{18}H_{22}$ (2 compounds), $C_{19}H_{24}$, $C_{21}H_{26}$, and $C_{15}H_{12}$. This last compound was definitely identified as methylanthracene. Donath¹⁹³ had previously claimed to have indicated the presence of this compound in a coal extract by the use of color reactions.

Hofmann and Damm pointed out that the unsaturated hydrocarbons isolated by them differed somewhat from those of Pictet, but were probably partially reduced polynuclear aromatic compounds (naphthalene, anthracene, etc.). The exact chemical nature of these compounds isolated was not clear but appears to include paraffins, bi-, tri-, and polycyclic naphthenes and their derivatives, diphenyl derivatives, and partially hydrogenated and substituted aromatic compounds.

Berl and Schildwächter¹⁹³ extracted two high-volatile bituminous coals with tetralin in an autoclave at 250° C and obtained yields of 20.3 and 16.6 percent, respectively. The extract from one of them was found to contain 1.43 percent acidic compounds (solid phenols), 0.034 percent bases, 7.84 percent asphaltic and resinous compounds, and 27.1 percent neutral oils (79 percent unsaturated). From the saturated hydrocarbon fraction of

the neutral oils, compounds having the formulas $C_{22}H_{46}$, $C_{24}H_{50}$, and $C_{30}H_{62}$ or $C_{30}H_{60}$, and, from the unsaturated fraction, compounds of the formulas $C_{12}H_{20}$, $C_{14}H_{22}$, $C_{15}H_{22}$, $C_{16}H_{22}$, $C_{17}H_{24}$, $C_{18}H_{24}$, $C_{19}H_{24}$, $C_{19}H_{26}$, $C_{19}H_{24}$, $C_{22}H_{28}$, $C_{25}H_{32}$, and $C_{26}H_{34}$ were isolated. Characterization of these compounds was on the basis of analysis and molecular-weight determinations.

The above work and that of others¹⁹⁴ represents only a few percent of the coal and tells nothing of the larger part of the coal mass itself or, for that matter, of a typical extract obtained under pressure. The large amount of hydrocarbon material does, however, suggest that units of structure containing the least oxygen are least firmly bound in the coal molecule.¹⁹⁵

In Asbury's first paper¹⁴⁶ he reported data which have served as a nucleus in obtaining a considerable amount of information on the specific constitution of Edenborn coal and very probably on other coals of similar rank. The material from the benzene pressure extractions was divided into acidic, basic, and neutral ether-soluble and -insoluble fractions. Table XLII is a summation of the results. With the exception of the extract from μ -coal, the total acids, bases, and phenols constituted less than 3 percent of the extract in comparison to the high-vacuum distillation of Edenborn coal which yielded about 12 percent of these materials.

The effect of heating on the chemical nature of the extract is shown in Fig. 11 and on a cumulative basis in Fig. 12. It will be noticed that there was a general rise in acidic, basic, phenolic, and neutral ether-soluble material with increasing tem-

¹⁹² Marcusson, J., and Böttger, F., *Ber.*, **57**, 633-5 (1924), consider melene to be a paraffin.

¹⁹³ Donath, E., *Z. angew. Chem.*, **19**, 657-68 (1906); *Chem.-Ztg.*, **43**, 497-9 (1910).

¹⁹⁴ Hackford, J. E., *Mining and Met.*, **163**, 35-6 (1920). Vener, R. A., and Oraľnikova, L. M., *Khim. Tverdogo Topliva*, **6**, 619-34 (1935); *Chem. Abs.*, **30**, 8566 (1936).

¹⁹⁵ Lowry, H. H., *Ind. Eng. Chem.*, **26**, 133-9, 320-4 (1934).

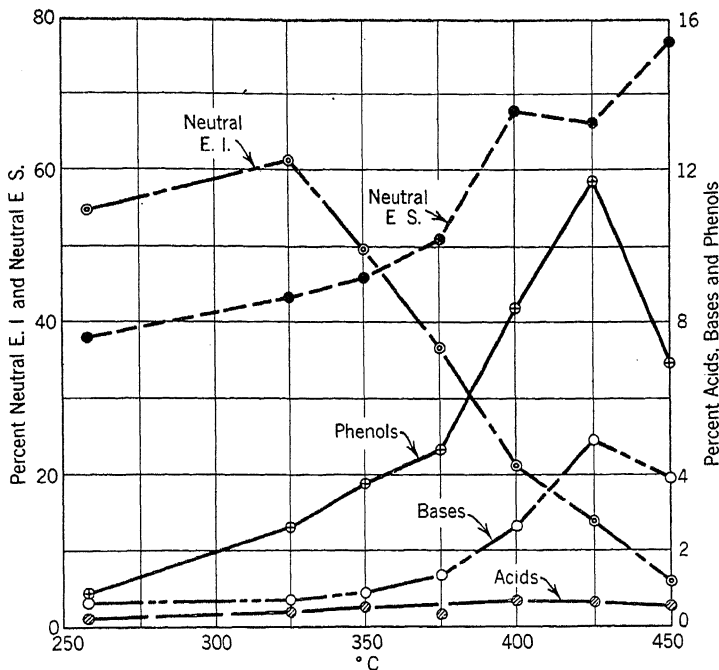


FIG. 11. Effect of temperature of heating on yield of extract constituents produced at each temperature (percentage in extract removed after each heating).¹⁴⁶

TABLE XLII

COMPOSITION OF EXTRACTS OBTAINED BY EXTRACTION WITH BENZENE¹⁴⁶

Coal size	4-8	16-20	60-80	
Temperature, °C	260	260	260	260
Total time of extraction, hours	47	44	38	302
Percent of extract as:				
acids	0.37	0.81	0.72	8.0
phenols	0.59	0.61	0.38	0.5
neutral:				
ether-insoluble	48.7	63.4	61.4	33.1
ether-soluble	36.7	30.4	36.3	60.2
Losses	11.8	4.13	0.67	-5.2

peratures up to 425°, after which a decrease in phenols, bases, and acids occurred. The neutral ether-insoluble material decreased with rising temperature, indicating the probable formation of acidic,

basic, and phenolic bodies from the neutral ether insolubles. These data and those in Table XLIII support the concept that the neutral ether-insoluble fraction of the ex-

TABLE XLIII

RELATION BETWEEN THERMAL TREATMENT AND YIELD OF NEUTRAL ETHER-INSOLUBLE MATERIAL¹⁹⁶

Treatment	Yield of Extract or Condensate, percent	Neutral Ether Insoluble Material, percent
1,000° C small tube furnace	15.2	0.27
527° C Fischer retort	17.63	2.78
527° C vacuum still	21.39	7.11
240° C benzene extraction	12.3	7.23

¹⁹⁶ Juettner, B., and Howard, H. C., *Contrib. S. Coal Research Laboratory*, 1933, 22 pp. Lowry, H. H., *J. Inst. Fuel*, 10, 291-301 (1937).

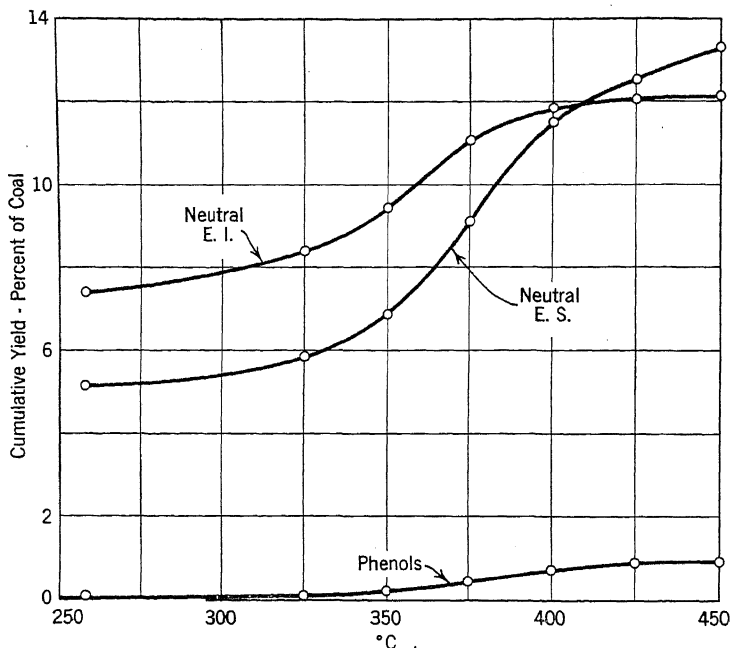


FIG. 12. Total cumulative percent of each extract constituent versus temperature (based on coal).¹⁴⁶

tract is an index of the primary degradation of the coal substance.

In Table XLII, the μ -coal showed a yield of phenolic and acidic material which was out of line with the other coal sizes. Asbury did not comment on this, but an explanation may be that the conversion of ether-insoluble to acidic materials was taking place slowly even at the low extraction temperature of 260° C, and, since the extraction time for the μ -coal was roughly 7 to 8 times as long as for the other sizes, a greater amount of acidic material would be formed. Note too that such a mechanism can explain away the inversion of the amount of neutral ether-soluble and -insoluble materials in going from the other particle sizes to the μ -coal.

In appearance the residue from the benzene extract resembled the original coal except for a slight decrease in luster. The

volume of pores less than 6μ in diameter was twice as great in the residues from the 260° C extraction as in the original coal.

In the extractions made by Asbury with aniline, tetralin, and phenol, the data given in Table XLIV were obtained.¹⁶⁴ It will be noted that there was a tendency for the phenols to increase with temperature while the ether insolubles decreased in amount.

The values for molecular weight are interesting in that they show the effect of temperature and the nature of the solvent. The molecular weights of the benzene extracts were in the neighborhood of 280¹⁹⁷ as determined in catechol.¹⁹⁸ Too much stress, however, should not be placed on

¹⁹⁷ Howard, H. C., *J. Phys. Chem.*, **40**, 1103-12 (1936).

¹⁹⁸ Smith, R. C., and Howard, H. C., *J. Am. Chem. Soc.*, **57**, 512-6 (1935), **58**, 740-2 (1936).

TABLE XLIV

COMPOSITION OF EXTRACTS WITH VARIOUS SOLVENTS ¹⁶⁴

Solvent	Aniline	Tetralin				Phenol
Temperature of extraction, °C	225	250	300	350	400	250
Total extract, percent	47	33.8	17.0	30.8	3.9	66.7
Composition of extract:						
acids	0.07	1.2	0.9	0.6	0.3	0.2
bases	1.30	0.5	0.4	0.6	1.1	0.2
phenols	0.48	0.9	1.0	1.8	2.0	1.0
ether solubles	12.78	38.2	25.5	31.3	69.2	10.5
ether insolubles	95.40	59.2	72.3	65.7	27.4	86.4
Molecular weight of ether insolubles	354	305	407	293	205	358

these values since it has never been firmly established whether the extracts were in true solution or partially in solution and partially in colloidal suspension. This applies both to the original solution during extraction and to that in the cryoscopic solvent. Considerable variation takes place in the molecular-weight measurements, depending on the cryoscopic medium, the strongly polar solvents such as catechol giving the lowest values. This again is evidence for depolymerization of the coal bitumens in the solvent. The low molecular weights of these extracts are not in agreement with their physical properties since they cannot be distilled *in vacuo* consistent with the behavior of certain other coal products and polymers.^{197, 198, 199, 200}

Biggs²⁰⁰ separated the extract obtained by Asbury into fractions: I, soluble in cold petroleum ether; II, insoluble in cold petroleum ether but soluble in ethyl ether after exhaustive extraction in a Soxhlet; and III, insoluble in ethyl ether. Fraction I contained hydrocarbons which made up about 2.3 percent of the coal, and since similar material had already been studied by others it was not investigated. The

molecular weights of II and III were approximately the same in catechol (285), but, in diphenyl, II gave a value of 470 and III a value greater than 1,000. The fact that the catechol values were about the same is evidence that the two fractions differed more in molecular size or degree of association than in chemical nature. Similar conclusions can be drawn from Weiler's work²⁰¹ on the halogenation of coal, extract, and residue, from the work of Biggs²⁰² on the hydrogenation and oxidation of extract and residue, and from the work of Kasehagen¹⁹⁹ on the alkali treatment of coal and extract. The extracts studied by these investigators were freed of petroleum-ether-soluble material. Hydrogenation of fractions II and III also indicated their similarity since, when the products were considered separately, no differences could be detected. The material from the hydrogenation was made up almost exclusively of entirely or partially hydrogenated aromatics. Dehydrogenation yielded products, again aromatic, containing monocyclic, bicyclic, and higher ring systems. The following hydrocarbons were isolated and definitely identified: $C_{10}H_8$ (naphthalene), $C_{11}H_{10}$ (β -methylnaphtha-

¹⁹⁹ Kasehagen, L., *Ind. Eng. Chem.*, **29**, 600-4 (1937).

²⁰⁰ Biggs, B. S., *J. Am. Chem. Soc.*, **58**, 484-7 (1936).

²⁰¹ Weiler, J. F., *Fuel*, **14**, 190-6 (1935).

²⁰² Biggs, B. S., *J. Am. Chem. Soc.*, **58**, 1020-4 (1936).

lene), $C_{12}H_{12}$ (two found, thought to be dimethylnaphthalenes), $C_{16}H_{10}$ (isomeric with pyrene but apparently not this compound), and $C_{18}H_{16}$. It was further shown by Biggs that the oxygen of the extract was neither carboxyl, methoxyl, nor carbonyl. Some hydroxyl oxygen was present, and by elimination it was indicated that one-fourth of the oxygen of II and three-fifths of that of III must occur as ether linkages or in heterocycles. It was also shown by Biggs²⁰² that the pseudo-bitumens obtained by the hydrogenation of the benzene pressure residue had properties in close agreement with those of the bitumens obtained with solvents.

Because of its remarkable solvent effect on bituminous coal, pyridine has been studied by a large number of investigators. Bedson²⁰³ studied the effect of this solvent and found that Manjok coal from Barbados was completely soluble, a New Zealand coal was 10 to 13 percent soluble, and anthracite was completely insoluble. From a study of six coals, Bedson concluded that there was no apparent relationship between yield of pyridine extract (22.5 to 32.2 percent) and either their gas-forming properties or their yield of volatile matter. Wahl,²⁰⁴ also working with pyridine, published a similar conclusion. It has been reported²⁰⁵ that both the amount of the pyridine extract and its chloroform-soluble part of 16 Chinese coals increased up to the point where the ratio of fixed carbon to volatile matter plus moisture was equal to 1.9, and then decreased. Baker²⁰⁶

extracted several coals with this solvent and obtained practically no yield from a South Wales anthracite, 20.4 percent from a Durham gas coal (Hutton Seam), 11.5 percent from a Durham coking coal (Brockwell), and 15.65 percent from a New Zealand brown coal (Ambrite). On the basis of the methods of Bedson, Anderson and Henderson²⁰⁷ extracted coals of Bengal and Japan and obtained 7 to 21 percent yield. A South African coal²⁰⁸ has been reported to be 15.4 percent soluble in this solvent. The extraordinary solvent power of pyridine is clearly indicated in the above work, which was carried out at the boiling point.²⁰⁹

Wheeler and his coworkers have developed the use of this solvent and have divided the extract into fractions according to its solubility in chloroform. The authors first stated:

We consider this method of treating coal—extraction with pyridine followed by extraction of the pyridine extract with chloroform—makes a complete or nearly complete, sep-

(1901); *Trans. North Engl. Inst. Mining Mech. Engrs.*, **50**, (2) 23-6 (1901); *Trans. Inst. Mining Engrs. (London)*, **20**, 159-63 (1901).

²⁰⁷ Anderson, W. C., and Henderson, J. A. R., *J. Soc. Chem. Ind.*, **21**, 237-43 (1902).

²⁰⁸ Robertson, J. B., *J. S. African Chem. Inst.*, **6**, No. 1, 20-30 (1923); *Chem. Abs.*, **17**, 1877 (1923).

²⁰⁹ See also: Fischer, F., and Schrader, H., *Ges. Abhandl. Kenntnis Kohle*, **4**, 360-2 (1919). Tawada, K., *J. Fuel Soc. Japan*, **7**, 41-7 (1928); *Chem. Abs.*, **22**, 3278 (1928). Lebeau, P., and Leroux, H., *Ann. combustibles liquides*, **5**, 443-54 (1930). Kopeliovich, N. A., and Kagan, E. D., *Khim. Tverdogo Topliva*, **3**, 32-8 (1931); *Chem. Abs.*, **28**, 5628 (1934). Sinnatt, F. S., *Proc. S. Wales Inst. Engrs.*, **47**, 793-825 (1932). Drees, K., and Kowalski, G., *Brennstoff-Chem.*, **15**, 221-9, 261-6 (1934); *Fuel*, **13**, 366-70 (1934), **14**, 18-23 (1935). Kuznetsov, M. I., and Nesterenko, L. L., *Khim. Tverdogo Topliva*, **8**, 222-32 (1937); *Chem. Abs.*, **32**, 1428 (1938). Müller, W. J., Graf, E., and Gruber, R., *Sparwirtschaft*, **15**, 198-9, 243-5 (1937). Roy, K. L., Lahiri, D., and Guha, B. C., *Ind. News Ed., J. Indian Chem. Soc.*, **1**, 95-108 (1938); *Chem. Abs.*, **33**, 833 (1939). Belcher, R., *Fuel*, **19**, 208-6 (1940).

²⁰³ Bedson, P. P., *J. Soc. Chem. Ind.*, **18**, 738-41 (1899); *Trans. North Engl. Inst. Mining Mech. Engrs.*, **48**, (3) 82-7 (1899); *Trans. Inst. Mining Engrs. (London)*, **16**, 388-93 (1899); *J. Soc. Chem. Ind.*, **27**, 147-50 (1908); *J. Gasbeleucht.*, **51**, 505 (1908).

²⁰⁴ Wahl, A., *Compt. rend.*, **154**, 1094-7 (1912).

²⁰⁵ Ping, K., *Bull. Geol. Survey China*, **23**, 21-30 (1933); *Chem. Abs.*, **28**, 3216 (1934).

²⁰⁶ Baker, T., *J. Soc. Chem. Ind.*, **20**, 789-90

aration between the resinous constituents and the degradation products of the cellulose of which coal is conglomerated.²¹⁰

Later¹⁶¹ the various fractions were designated as α , β , and γ and described as follows:

α Fraction, insoluble in pyridine consisting of undispersed ulmins plus resistant plant remains.

β Fraction, soluble in pyridine but insoluble in chloroform consisting of dispersed ulmins.

γ Fraction, soluble in both pyridine and chloroform consisting mainly of resins and hydrocarbons.

More recently²¹¹ it has been reported that "this separation of α , β , and γ fractions from coal is only a means to an end and has no absolute significance."

That the γ fraction contained resinous material was believed to have been established²¹² by the fact that both this material and true resins affected a photographic plate after the method of Russell.²¹³ It would correspond closely to the petroleum-ether-soluble fractions of Bone¹²⁴ and Fischer.¹⁴⁸ The α and β fractions were indicated to be chemically similar as shown by their analysis (Table XLV) and volatile products on pyrolysis.¹⁶¹ Similarity between the α and β components was also indicated in the actual analysis of the volatile constituents at temperatures ranging from 600 to 1,000° C. The hydrocarbons resulting from thermal decomposition of the γ fraction were much greater in amount than those from either the α or the β fraction. While the hydrogen from the α or β fractions was greater

TABLE XLV

ANALYSIS OF α , β , AND γ FRACTIONS IN PERCENT ON ASH-FREE BASIS¹⁶¹

	Pyridine Insoluble, α	Pyridine-Soluble, Chloroform-Insoluble, β	Pyridine-Soluble, Chloroform-Soluble, γ
Volatile matter	34.96	31.88	77.33
Fixed carbon	65.04	68.12	22.67
Carbon	80.81	77.32	85.33
Hydrogen	5.23	5.14	7.08
Oxygen	10.40	14.26	4.56
Nitrogen	2.14	2.07	1.71
Sulfur	1.42	1.21	1.32

than that from the γ fraction, Jones and Wheeler²¹⁴ reported a coal (Durham) which gave no hydrogen at all from the γ fraction, whereas the α and β yielded 14.8 and 19.1 percent respectively upon low-temperature carbonization. It is interesting that the γ fraction gave no phenols upon carbonization, whereas both the α and β constituents produced considerable quantities. The similarity of the α and β has been further demonstrated by Pearson,²¹⁵ who treated both fractions with fuming sulfuric acid to obtain products which he called "oxahumins." The progressive changes in the formation of these bodies indicated a strong resemblance between the two fractions. X-ray diffraction studies by Mahadevan²¹⁶ have also indicated the similarity between α and β fractions and the original coal. On the other hand, the γ fraction was shown to differ. Patterns obtained with this material resembled, but were more complex than, those obtained with natural and fossil resins.

²¹⁰ Burgess, M. J., and Wheeler, R. V., *J. Chem. Soc.*, **99**, 649-67 (1911).

²¹¹ Wheeler, R. V., *J. Soc. Chem. Ind.*, **50**, 550-4 (1931).

²¹² Clark, A. H., and Wheeler, R. V., addendum with Platt, C. B., *J. Chem. Soc.*, **103**, 1713-5 (1913).

²¹³ Russell, W. J., *Proc. Roy. Soc. (London)*, **B80**, 376-87 (1908).

²¹⁴ Jones, D. T., and Wheeler, R. V., *J. Chem. Soc.*, **107**, 1318-24 (1915), **109**, 707-14 (1916).

²¹⁵ Pearson, A. R., *J. Soc. Chem. Ind.*, **42**, 68-72T (1923).

²¹⁶ Mahadevan, C., *Indian J. Physics*, **4**, 79-98 (1929), **5**, 525-41 (1930); *Fuel*, **14**, 231-41 (1935).

Cockram and Wheeler²¹⁷ investigated the γ fraction somewhat in detail and adopted the subfractions: γ_1 soluble in light petroleum, mainly hydrocarbon; γ_2 soluble in ethyl ether, reported to be resins, resins, and resenes; γ_3 and γ_4 insoluble in ethyl ether which were simply "resinlike." Oxidation of these fractions with hydrogen peroxide indicated that γ_2 , γ_3 , and γ_4 were different in nature; however, oxidation with nitric acid showed resemblances between them.

Extraction with pyridine involves several important factors. First, the presence of an inert atmosphere appears to be absolutely necessary,^{218, 219} and the extraction must be carried out in the absence of moisture^{218, 220} if the maximum yield of extract is to be obtained. Second, the pyridine is extremely difficult to remove from the extract and residue. Even washing with hydrochloric acid does not appear to remove all of it. Practically every worker who has used this solvent reports the tenacious manner in which pyridine is held by the extraction products. Some have considered the possibility of the formation of a molecular complex between the coal and solvent. Pearson²¹⁵ thought that only the resinic part of the coal was dissolved and the remaining apparently soluble material (humic) was in reality dispersed as colloidal aggregates. In support of this theory he cited the following:

1. That the humic material (ultra-humins), when isolated, tenaciously re-

tained pyridine, which was removable at a slow but constant rate in a vacuum.

2. That the ultrahumins behaved like an irreversible colloid since when the pyridine was finally and completely removed only about 10 percent of the material could be redispersed in the pyridine.

3. That another solvent would displace the pyridine adsorbed on the surface of the ultrahumins.

With respect to this last point it has been reported²²¹ that xylene can be used to replace pyridine. The experimental procedure consisted in evaporating the pyridine-extract mixture to a small volume and adding increments of xylene and distilling again to a small volume after each addition. It was claimed that this process completely removed all traces of pyridine from the extract.

The opinion, frequently expressed, that pyridine does not act as a simple solvent but rather brings about a colloidal dispersion of the coal substance is based on the re-solution behavior of the extracts referred to above and the similarity between the ultimate analysis of the extract, residue, and original coal. It was found in the work conducted at the Coal Research Laboratory,¹⁶⁵ in which the extracts from a large number of solvents were studied, that re-solution of the extracts from practically all the solvents was interfered with both by oxidation and by prolonged heating in *vacuo* at moderate temperatures (about 100° C) such as would be necessary to remove a solvent. This is undoubtedly a repolymerization phenomenon. Examination of a large number of analyses has sometimes shown a similarity between carbon and hydrogen content, but at the same time a nitrogen value which indicates in-

²¹⁷ Cockram, C., and Wheeler, R. V., *J. Chem. Soc.*, **130**, 700-18 (1927), **134**, 854-60 (1931).

²¹⁸ Bone, W. A., and Sarjant, R. J., *Proc. Roy. Soc. (London)*, **A96**, 119-36 (1919). Bone, W. A., Pearson, A. R., Sinkinson, E., and Stockings, W. E., *ibid.*, **A100**, 582-98 (1923).

²¹⁹ Chatterjee, N. N., *Quart. J. Geol. Mining Met. Soc. India*, **2**, 89-95 (1929); *Chem. Abs.*, **25**, 5003 (1931).

²²⁰ Mackenzie, K. G., *Ind. Eng. Chem.*, **1**, 360-2 (1909). Malanowicz, L., *Chimie & Industrie*, **28**, 1277-82 (1932).

²²¹ Kester, E. B., *U. S. Bur. Mines, Circ.* **6486** (1931), 17 pp.

complete removal of the pyridine. Retention of pyridine by the extract would tend, generally, to lower the carbon content (pyridine contains 76 percent carbon). Analyses reported by other authors, however, do not show such similarities, and it is not likely that invariably the analysis is at fault as claimed by Kuznetsov.¹⁷⁷ It can hardly be questioned that the low-molecular-weight hydrocarbons extracted are in true solution, and, since the amount of this material varies from one coal to another, departures from an analysis which would indicate colloidal dispersion would be found, depending on the content of these substances. Then, too, if the action of pyridine were simple peptization, one might expect to find a resemblance between the ash content of coal, extract, and residue. This, however, is not found.

The object here has not been to question the colloidal dispersion of coal in pyridine but to point out that the above observations do not constitute good arguments for so considering it. As a matter of fact, a number of things might indicate that it is. The very chemical nature of the solvent should be evidence that it would tend to produce colloidal dispersions. Physical behaviors, such as the remarkable swelling of the coal, the gelatinous appearance of the residue, and the viscosity of the extract solution which is maintained even after considerable dilution, are all indications of a colloidal system. Examinations of the extract solution for colloids are not very significant since the particles might have been precipitated during concentration of extract in the solvent when a Soxhlet extraction is made or upon cooling in a bomb type of extraction.

The extraction of coal has been considered as a colloidal dispersion process by in-

vestigators who used pyridine,^{155, 215, 222, 223} aniline,^{155, 223} quinoline,^{155, 223} isoquinoline,¹⁵⁵ tetralin,^{155, 223} decalin,¹⁵⁵ phenols and primary tar fractions,^{155, 223} *p*-nitroaniline,¹⁵⁵ nitrobenzene,¹⁵⁵ acetone,¹⁵⁵ anthracene oil,²²³ and mixtures^{155, 223} as solvents. The use of "heavy solvents" such as anthracene oil, naphthols, olein (crude oleic acid?), or mixtures of anthracene oil and olein²²⁴ to bring about the "complete" solution of coal at rather high temperatures (200 to 400° C) is probably a colloidal dispersion behavior and appears to be so considered by Gillet and coworkers. Pertierra²²⁵ has stated that the ash content of the extract, which is practically nil at 230° C, increases with rise in temperature of extraction, which again is good evidence of colloid formation.

A few attempts have been made to develop practical uses for pyridine as a sol-

²²² Tideswell, F. V., *Trans. Inst. Mining Engrs. (London)*, **76**, 171-88 (1930). Piettre, M., *Compt. rend.*, **177**, 486 (1923).

²²³ Pertierra, J. M., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 13-6 (1931); *Anales soc. españ. fis. quim.*, **29**, 663-79 (1931), **31**, 271-88 (1933), **32**, 702-26 (1934); *Fuel*, **13**, 23-6 (1933); *Chaleur et ind.*, **15**, No. 167, 442-5 (1934); *J. Inst. Fuel*, **9**, 16-23 (1935); *15me Congr. chim. ind. (Bruxelles, September, 1935)*, **1936**, 377-82; *Ile Congr. mondial petrole*, **2**, Sect. 2, *Phys. chim. raffinage*, 213 (1937).

²²⁴ Rütgerswerke Akt.-Ges., Ger. Pat. 320,056 (1918); Brit. Pat. 131,588 (1919). Von Skopnik, A., *Teer*, **24**, 358-60 (1926). Gillet, A., *Chimie & industrie*, **1931**, Spec. No., 295-301; *Proc. Intern. Conf. Bituminous Coal*, **2**, 1-12 (1931); *Brennstoff-Chem.*, **17**, 421 (1936); *Bull. soc. chim. Belg.*, **47**, 813-7 (1938). Gillet, A., and Pirlot, A., *ibid.*, **41**, 511-20 (1932), **43**, 1-24 (1934), **44**, 504-12 (1935), **47**, 518-24 (1938). Coninx, L., *Bull. sci. assoc. élevés écoles spéciales univ. Liège*, **1933**; *Fuel*, **14**, 180-1 (1935). Gillet, A., Pirlot, A., and Coninx, L., *Bull. soc. chim. Belg.*, **43**, 382-91 (1934). Gewerkschaft Mathias Stinnes, Brit. Pat. 464,337 (1936). Gillet, A., Pirlot, A., and Desirrotte, L., *15me Congr. chim. ind. (Bruxelles, September, 1935)*, **1936**, 267-75. Gillet, A., Pirlot, A., and Monfort, F., *Bull. soc. chim. Belg.*, **47**, 525-31, 809-12 (1938).

²²⁵ Pertierra, J. M., *15me Cong. chim. ind. (Bruxelles, September, 1935)*, **1936**, 377-82.

vent. Dennstedt and Bünz²²⁶ showed that for the six coals which they studied the spontaneous combustibility of the dust increased with the yield of pyridine extract. Wheeler,²²⁷ in agreement with this, reported that, although there was no apparent relation between volatile matter and inflammability of coal dust for a large number of coals studied, there was a tendency for the ignition temperature of the dust to increase with decrease in the amount of pyridine soluble material. Nübling and Wanner²²⁸ reported data which showed a definite increase in ignition temperature with decrease in yield, but their work was limited to only three coals. Harger¹⁵⁹ mentioned the fact that, whereas the British Government Experimental Station had found a relation between the inflammability of coal dust and the yield of pyridine extract, the chemists of the French Government had not. Whether this difference was due to the coals or to the experimental procedures could not be determined from the information at hand. A possible contribution to the problem of spontaneous combustion of coal has been made by Graham and Hill,¹⁷⁵ who found that the ability to absorb oxygen resided almost entirely in the residue left from the pyridine extraction.

The Wheeler school has proposed the use of pyridine in determining the "rational analysis" of coal in terms of the proportions of free hydrocarbons, resinous compounds, organized plant entities (spore exines and cuticular tissues), and ulmin compounds which it contains.²¹⁷ It was their belief that only the last-named component changed to any extent with pro-

gressive coalification as indicated by the decrease in its solubility in alkali with age of the coal. A preliminary study of a number of coals suggested that a measure of the difference in characteristics between the ulmins of two coals could be obtained by determining their reactivity, for example, from the proportion rendered soluble in alkali after their oxidation under standard conditions. Such a measure was referred to as a "reactivity index." Data²²⁹ given for Pittsburgh Seam coals indicated a general relationship between the carbon content of the coal and the reactivity index. Better agreement was obtained between the index and carbon content of the vitrain than with the coal as a whole, possibly because vitrain is essentially free of plant entities and can also be easily freed of mineral matter. Later²³⁰ a somewhat more refined and rapid procedure was reported, and data were cited for English coals. In general, efforts to relate rank of a coal to its yield of extract have not been successful. Cockram and Wheeler²¹⁷ concluded, after a study of Pittsburgh and Barnsley Seam coals, that there was no evidence of progressive change in any constituent with increasing rank, in opposition to the opinion of Fischer, Broche, and Strauch¹⁴⁸ that there was an increase in free hydrocarbon content with increase in rank. Bone²¹⁸ tried to find a relation between the amount of coal soluble in pyridine and volatile matter but concluded after the study of two coals that there was none. Kester, Schneider, and Jung²³¹ studied a large number of American coals

²²⁹ Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **131**, 2967-79 (1928).

²³⁰ Wheeler, R. V., *Gas World*, **94**, Coking Sect., 51-5 (1931); *Colliery Guardian*, **142**, 1877 (1931). Francis, W., and Wheeler, R. V., *J. Chem. Soc.*, **134**, 586-93 (1931).

²³¹ Kester, E. B., Schneider, E. J., and Jung, F. W., *Ind. Eng. Chem., Anal. Ed.*, **6**, 98-103 (1934).

²²⁶ Dennstedt, M., and Bünz, R., *Z. angew. Chem.*, **21**, 1825-35 (1908).

²²⁷ Wheeler, R. V., *J. Chem. Soc.*, **103**, 1715-22 (1913).

²²⁸ Nübling, R., and Wanner, H., *J. Gasbeleucht.*, **58**, 515-8 (1915).

for which data were available^{147, 149, 232} on both the amount of α , β , and γ constituents and the oily and solid bitumens and found no apparent relationship between the amount of volatile matter of the coal and the amount of pyridine-soluble material.

The claim has been made that pyridine vapor is absorbed by coal to an extent depending on its age and petrographic constituents. Young coals have been reported to absorb the vapor rapidly, whereas older coals absorbed very little. Also, vitrain absorbed the most and fusain the least amount of vapor. Several studies²³³ have been reported which indicate that, among the numerous coals considered, the greater number show a relationship between age, or rather degree of polymerization as indicated by the carbon-to-hydrogen ratio,²³⁴ and amount of vapor absorbed. The interesting thing about this work is the fact that the amount of vapor absorbed seems to be related to the amount of pyridine extract, which would then indicate a relationship between rank and yield of extract in opposition to the findings of Wheeler and Bone reported earlier and those of Malanowicz,²²⁰ who reported no appreci-

able connection between the extractability of coal and its power to absorb pyridine vapor.

Wahl and Bagard²³⁵ have used pyridine to study the structure of coal. Samples of various coals were polished and immersed in pyridine for several hours. A coal from Lens which was practically insoluble in the solvent showed no structure, whereas another coal which gave 19.3 percent of extract showed granular bands on its surface, the existence of which was not previously noticeable. Stopes and Wheeler²³⁶ have reported the use of the solvent vapor in a similar application.

Further work has been carried out with other basic solvents. Bone,²¹⁸ comparing the yields with pyridine (b.p. 115° C) and the homologous picolines (b.p. 130 to 150° C), found that approximately the same quantity of material was removed at the boiling points. On the other hand, if pyridine was used under pressure at 130 to 150° C more than double the quantity of extract was obtained. Malanowicz²²⁰ reported that the picolines had a higher solvent power than pyridine as a result of their higher boiling points. Kuznetsov's work (Table XXXVII) indicated that pyridine was the superior solvent when boiling points are taken into consideration. There is little chance of drawing any definite conclusion since the procedures and coals studied by these authors differed. Vignon²³⁷ studied the action of aniline (b.p. 184° C) and quinoline (b.p. 238° C) and reported the yield with quinoline (47.3 percent) to be three times that with pyridine and twice that with aniline (23.4 per-

²³² Fieldner, A. C., Davis, J. D., Kester, E. B., Selvig, W. A., Reynolds, D. A., and Jung, F. W., *U. S. Bur. Mines, Tech. Paper* **511** (1932), pp. 33-4, **543** (1932), pp. 3-4. Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *ibid.*, **519** (1932), pp. 45-6, **524** (1932), p. 51, **531** (1932), pp. 17-21, **542** (1932), pp. 30-1, **548** (1933), pp. 29-30.

²³³ Chorazy, M., *Przemysł Chem.*, **15**, 233-52, 257-70 (1931); *Chem. Abs.*, **26**, 1750 (1932). Bunte, K., Brückner, H., Simpson, H. G., *Fuel*, **12**, 222, 268-70 (1933), **14**, 350-2 (1935).

²³⁴ Tideswell, F. V., *Fuel*, **1**, 244-7 (1922), questioned the relationship between carbon-to-hydrogen ratio and degree of polymerization. As a matter of fact this author objected to the use of the term "depolymerization" as applied to the action of pyridine but suggested a mechanism which sounds very much like an argument for depolymerization.

²³⁵ Wahl, A., and Bagard, P., *Compt. rend.*, **157**, 380-1 (1913).

²³⁶ Stopes, M. C., and Wheeler, R. V., *Fuel*, **3**, 63-7 (1924).

²³⁷ Vignon, L., *Compt. rend.*, **158**, 1421-4 (1914); *Ann. chim.*, **13**, 284-301 (1920).

cent). Staemmler²³⁸ has reported a coal which was 53.3 percent soluble in aniline at the boiling point.

Many investigators have found that oxidation tends to reduce the amount of soluble material in coal, and it has been suggested that extraction might be used as a method of detecting the extent of weathering.²³⁹ Relatively little has been done to investigate the possibility of such tests, and it is probably necessary that a thorough study be made, since, though most authors report a decrease in yield upon oxidation,^{153, 240} at least two^{126, 241} have given data for coal which actually showed an increased yield after oxidation. Of the three coals studied by Agde and Winter,²⁴¹ two decreased and one increased in the amount of benzene pressure extract yielded after the coal had been oxidized. It was found that the yield of "Ölbitumens" (petroleum-ether-soluble) increased in all three coals, while the "Festbitumens" (petroleum-ether-insoluble) decreased. All the Fest- to Ölbitumen ratios were lessened, that of the coal with the highest cakability being least affected. Moreover, the decomposition temperatures of the Festbitumens were all lowered, and again the effect was least marked in the coal of highest cakability.

A small amount of work has been reported, in addition to that already mentioned, on the extraction of the petrographic constituents of coal. Application

of Wheeler's²⁴² method of solvent analysis gave the data reproduced in Table XLVI (Hamstead Seam coal).

TABLE XLVI

YIELDS * IN PERCENT FROM THE PETROGRAPHIC CONSTITUENTS OF HAMSTEAD SEAM COAL WITH VARIOUS SOLVENTS²⁴²

Solvent	Vitrain	Clarain	Durain	
Pyridine	34.4	27.2	21.6	10.1
Alcohol	6.6	5.7	3.1	
Chloroform	2.85		2.4	
Pyridine extract soluble in chloroform	27.0	30.0	40.0	
α Compounds in coal	65.8	72.8	78.4	
β Compounds in coal	25.0	19.0	13.0	
γ Compounds in coal	9.2	8.2	8.6	

* On dry, ash-free basis.

Several interesting points are noticeable in this table. Vitrain, clarain, and durain appear to contain the same, or approximately the same, proportion of " γ compounds"; the chief difference, therefore, in the composition of banded coal would seem to lie in the α and β compounds. Considerable evidence has been reported which indicates the α and β fractions to be chemically similar; hence, it might be inferred that the main difference between vitrain and durain and possibly clarain is a physical one and involves a distinction of degree rather than kind. Broche and Schmitz¹⁴¹ extracted vitrain and durain samples which were 91.5 and 93.6 percent petrographically pure with benzene under pressure and obtained yields of 11.8 and 14.1 percent. These values are too close to admit the possibility of any great difference in nature of the constituents. Bone and Bard²⁴³ reported that bright, dull, and fusain constituents which they ex-

²³⁸ Staemmler, C., *Brennstoff-Chem.*, **11**, 281-2 (1930).

²³⁹ Mendelsohn, J., *J. Chem. Met. Mining Soc. S. Africa*, **33**, 285-9 (1933).

²⁴⁰ Voitova, E. V., *Brennstoff-Chem.*, **16**, 21-4 (1935). Gusinskaya, S. A., and Baskina, E. I., *Coke and Chem. (U.S.S.R.)*, No. 1, 60-8 (1934); *Chem. Abs.*, **29**, 3492 (1935).

²⁴¹ Agde, G., and Winter, A., *Brennstoff-Chem.*, **15**, 67-8 (1934).

²⁴² Tideswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **115**, 619-36 (1919). Stopes, M. C., and Wheeler, R. V., *Fuel*, **2**, 83-92 (1923).

²⁴³ Bone, W. A., and Bard, B. J. A., *Proc. Roy. Soc. (London)*, **162A**, 495-501 (1937).

tracted with benzene all gave the same yield for the same coal.

Beet,²⁴⁴ on the other hand, examined a number of coals and investigated the solubility of the original coal and the fusain. It was found that the fusain was much less soluble than the original coal (of the order of a tenth) except in a few samples where poor technique had led to contamination of the fusain sample. Unfortunately no attempt was made to separate the coal further or to make a solvent study of the constituents. It has been shown²⁴⁵ that, with increased coalification of the bright coal, the γ_2 and β bitumens increased, permanganate numbers of original and extracted coal decreased, the total pyridine bitumens increased, and the softening and decomposition points of the bitumens rose. Bertrand²⁴⁶ extracted samples of coal with anthracene and olein for varying periods of time. The residue after the extraction was impregnated with carnauba wax and polished. Subsequent examination showed that the vitrain could be almost completely removed; the clarain could be extracted in part, and the durain and fusain remained unaffected. The durain, it was found, could be removed by the solvent under pressure.

A very large part of the literature of solvent extraction treats of the search for a hypothetical coking principle. To consider each paper separately would be not only a long but also a profitless task since the greater part of the reported data cannot be placed on a comparative basis. Controversy which has always existed in this field can be traced to differences in experimental procedures and lack of a

standard definition of what constitutes a coke.

DeMarsilly²⁴⁷ noted as early as 1862 that the residue obtained in the extraction of coal with alcohol, ether, carbon disulfide, benzene, and chloroform gave a poorer coke upon heating than the original coal. Siepmann¹⁸⁵ used three of these solvents and reported that in his opinion the caking power of the coal was not due to, but influenced by, the soluble constituents. Anderson,²⁴⁸ in contradiction to the work of DeMarsilly, found no apparent change in the coking properties of coal after extraction with a high-boiling petroleum ether fraction or with carbon disulfide. Later Baker²⁰⁶ reported that extraction of a coal with pyridine destroyed its coking properties, but the extract gave a very intumescent coke. Other investigators who have made extractions with pyridine,^{203, 249, 250} cresol,²⁵⁰ aniline,^{237, 251} and tetralin^{112, 163, 252} have reported data which

²⁴⁷ Occasionally this work of DeMarsilly, *DeC., Ann. chim. phys.*, (3), **66**, 167-71 (1862), is reported to be the first attempt to extract coal with solvents. In addition to the several earlier papers already cited, two others are known: Schrotter, A., *Sitzber. Akad. Wiss. Wien Math. Naturw. Klasse*, **3**, 285-87 (1849); Wackenroder, H., *Arch. Pharm.* **110**, 12-27 (1849).

²⁴⁸ Anderson, W. C., *Trans. Glasgow Phil. Soc.*, **29**, 72-96 (1897); *Trans. Inst. Mining Engrs. (London)*, **16**, 335-58 (1899).

²⁴⁹ Wahl, A., *Bull. soc. ind. minérale*, **100**, (1912); *Bull. soc. chim.*, **21**, 76 (1917); *Compt. rend.*, **154**, 1094-7 (1921). Hankiss, S., *Szenkiserleti Közlemenyek*, **2**, 57-66 (1927); *Chem. Zentr.*, **1929**, II, 672. Massinon, J., *Bull. soc. belge ing. ind.*, 20-34 (1935); *Chem. Abs.*, **29**, 4157 (1935). Chatterjee, N. N., *Quart. J. Geol. Mining Met. Soc. India*, **6**, 99-111 (1934); *Chem. Abs.*, **29**, 5249 (1935).

²⁵⁰ Lefebvre, H., *Chimie d industrie*, **1932**, Spec. No., 229-33.

²⁵¹ Shishkin, K. N., *Coke and Chem. (U.S.S.R.)*, **4**, 16-22 (1934); *Chem. Abs.*, **30**, 3203 (1936).

²⁵² Fujimura, K., *J. Soc. Chem. Ind., Japan*, **33**, Suppl. binding, 201-2 (1930); *Chem. Abs.*, **24**, 4374 (1930).

²⁴⁴ Beet, A. E., *Fuel*, **3**, 390-2 (1924).

²⁴⁵ Drees, K., and Kowalski, G., *Brennstoff-Chem.*, **15**, 261-6 (1934).

²⁴⁶ Bertrand, A., *Ann. soc. geol. Belg.*, *Bull.* **61**, 327-36, 337-52 (1937-8).

are in general agreement with those of Baker.

The papers of Novak and Hubacek¹¹² are of great interest in this connection. The coals studied (Czechoslovakian) were: (1) a brown coal from the Karoline Seam (26 percent yield); (2) a brown coal from the Hedvika Seam (24 percent yield); (3) a subbituminous coal from the Max Seam, noncoking (32 percent yield); and (4) a bituminous coal from the Jaroslav Seam, coking (30 percent yield). Extractions were carried out for 8 hours at about 300° C in an autoclave. Since 5 kilograms of coal and 10 liters of tetralin were heated together in this apparatus only once it is very probable that the extractions were by no means complete and hence the results must be looked on with some caution. After extraction, the extract was divided into six classes of substances according to solubility in various solvents. The most swollen cokes resulted when the inert material (powdered coke) was a minimum and the hardest when the ratio of inert to substance was 3:1. Any of the extractable materials which had a more or less distinct melting point were able to bind the inert material together to some extent. The liquid fractions of the noncoking and brown coals possessed this property to some degree. The authors pointed out the value of a "cementing residuum," i.e., the coherent residue left after the carbonization of the various fractions in determining the agglutinating powers of the fractions.

By means of curves the authors estimated the temperature range through which the bitumens remained in the liquid or plastic state and concluded that this range was greatest for coking coals. There is some merit to this idea, and it would be interesting to see it applied to more coals using a better extraction procedure.

Berl and Schildwächter¹⁶³ found that, when the bitumens from tetralin pressure extractions were separated into oily and solid fractions as in Fischer's method and then mixed with the residue and coked, the solid bitumens promoted swelling and the oily bitumens caused cementing to coke. Later, and this is important, they showed that, if the coking process was watched microscopically, the decomposition appeared more like that of the added bitumens than that of the original coal. The end of the coke formation and other noticeable changes all occurred about 100° lower with the mixture than with the original coal.

Berl and Koerber²⁵³ have published results obtained in the extraction of a Pittsburgh Seam coal, two artificial cellulose coals, and a lignin coal with organic solvents. Part of their data for the Pittsburgh coal are given in Table XLVII. These authors stated that the bitumen which distills off at higher temperatures in the coking process is the cause of sandy coke formation, but, if, on the other hand, the bitumens decompose below its boiling point to form large molecules which serve to cement the nonsoluble organic part of the coal, then hard cokes result. This mechanism is similar to that proposed by Novak and Hubacek.¹¹² Berl and Koerber expressed the opinion that polar solvents with partial valences on their oxygen atoms had a selective affinity toward the phenolic components of bitumen. These phenolic substances were thought to be responsible for the coking properties of coal. No data were given on the actual phenolic content of the extracts.

In addition to the work on the effect of pyridine extraction on coking already given, some information is available on the

²⁵³ Berl, E., and Koerber, W., *Ind. Eng. Chem.*, **32**, 1605-6 (1940).

TABLE XLVII

YIELD OF EXTRACT AND COKING PROPERTIES OF RESIDUE ²⁵³

Solvent	Temperature of Extraction °C	Weight of Extract percent	Coke of Residue	
			Appearance *	Yield percent
Acetone 1	20	0.3	+	64.4
	56.5	0.4	+	64.5
		0.7		
Benzene 1	20	0.01	+	64.2
	80	0.2	+	64.6
		0.21		
Dioxane 1	20	0.6	+	64.6
	100	0.4	+	63.8
		1.0		
Acetophenone 1	20	4.0	+	65.5
	100	18.6	—	71.9
		10.2	—	73.9
	205	32.8		
Tetralin, twice under pressure	300	18.8	+	—
Benzophenone	310	12.6	—	73.7

* Hard dense coke, + ; sandy coke, —.

effect of the α , β , and γ constituents. Cockram and Wheeler ²¹⁷ reported that a blend of these fractions in proportion to the amount in a coal gave a hard, well-sintered coke button very similar in appearance and strength to that obtained from the original coal. Blends were also tried of the α and β with γ_1 , γ_2 , γ_3 , and γ_4 fractions. The γ_1 and γ_2 fractions gave good cokes, that from γ_1 being the best, but both the γ_3 and γ_4 fractions gave non-coherent residues. Just a few years before, Foxwell ²⁵⁴ had published a paper reporting results completely contradictory to the above. He found that when the α , β , and γ were recombined and heated the resulting mixture did not form a coke. This he explained by assuming considerable changes in the structure of the coal upon extraction,

²⁵⁴ Foxwell, G. E., *Fuel*, **3**, 276-83, 315-19 (1924).

which indicated that the chief difference between coking and noncoking coal was a structural one. Cockram and Wheeler stated that the coking principle necessary for the production of a good coke is provided by the resins and hydrocarbons of the coal (γ fractions), ²⁵⁵ pointing out that the best coke was obtained with $\alpha + \beta + \gamma_1$ fractions. Other authors have published results which cannot be compared with, or are not in agreement with, these data. Several have reported, for example, that the γ_1 fraction is almost without effect when mixed with α alone, ²⁵⁶ or that the coking properties reside in the β , γ_3 , and γ_4 fractions and the α fraction diminishes them. ²⁵⁷ The γ_1 compounds are responsible for the agglutinating action and the γ_2 and γ_3 compounds afford swelling, according to Shimmura. ²⁵⁸

The importance of the residue has been shown by the report that the extract from a poor coal mixed with residue from a good coal gave a good coke whereas the extract from good coal mixed with the residue of a poor coal gave a poor coke. ²⁵⁹

Extraction studies made by Neumann and Kremser ²⁶⁰ indicated that the largest

²⁵⁵ Illingworth, S. R., *J. Soc. Chem. Ind.*, **39**, 111-8T (1920). Barash, M., *ibid.*, **48**, 174-83T (1929).

²⁵⁶ Schlöpfer, P., and Morecom, A. R., *Eidgenöss. Materialprüfungsanstalt E. T. H. Zürich Ber.*, No. 62 (1933), p. 60; *Schweiz. Ver. Gas- u. Wasserfach Monats Bull.*, **12**, 373-427 (1932); *Chem. Abs.*, **27**, 2282 (1933).

²⁵⁷ Bunte, K., *Österr. Ver. Gas- u. Wasserfach*, **71**, 81-90 (1931); *Fuel*, **11**, 400-5 (1932). Bunte, K., Brückner, H., and Sanjana, J., *Brennstoff-Chem.*, **16**, 50-2 (1935). Bunte, K., Brückner, H., and Simpson, H. G., *Fuel*, **12**, 222-32 (1933).

²⁵⁸ Shimmura, T., *J. Fuel Soc. Japan*, **11**, 140-9 (1932); *Chem. Abs.*, **27**, 2556 (1933).

²⁵⁹ Drees, K., and Kowalski, G., *Gas- u. Wasserfach*, **76**, 653-60 (1933).

²⁶⁰ Neumann, B., and Kremser, L., *Glückauf*, **69**, 813-20 (1933).

amount of coking constituents are found in the vitrain.²⁶¹

Kester, Schneider, and Jung²⁶¹ reported on the extraction of twenty coals with benzene and pyridine to give a re-solution of the bitumens, ulmins, and resistant plant residues. An attempt was made to correlate the properties and amounts of the fractions so obtained with the coke-forming properties of the coals. All such attempts were unsuccessful. Duparque and Massinon²⁶² studied coals from ten seams by extraction with benzene, chloroform, and pyridine; they concluded that coking properties of the coals could not be differentiated by extraction results.

Fischer and associates¹⁴⁸ have reported that when the oily and solid bitumens referred to earlier were individually coked with the residue the oily ones were found to be responsible for the cohesiveness of the button, and the solid brought about swelling. The importance of the decomposition point of the solid bitumens in the formation of a good coke was pointed out. Dolch²⁶³ examined a number of German coals and confirmed the work of Fischer on the influence of the two bitumens on coking behavior. Van der Waerden,²⁶⁴ on the other hand, found no relation between the bitumens and coking capacity of a bituminous East Indian coal.

Bone and coworkers^{85, 123} found that, contrary to the work of Fischer, the caking power of a coal lay largely in the part of the extract corresponding to Fischer's solid bitumens (fractions III and IV). Fractions I and II, though contributing little to the coking process, were not without influence.

Davis and Reynolds²⁶⁵ confirmed the work of Bone and described a third type of extractible material which they called insoluble bitumen. Broche and Bahr²⁶⁶ repeated the work of Fischer et al. and at the same time carried out experiments using the methods of Bone. These investigators arrived at the extraordinary conclusion that both the English and German workers had been correct. The discrepancy in results, they explained, lay in the use of powdered coke by Bone instead of the residue. Bone²⁶⁷ has pointed out that since Fischer did not use a Soxhlet type of extractor his residue still contained enough fraction IV to affect the results.

Another difference was not so easily explained. Bone had made a few tests using residue instead of coke and had obtained no intumescence with his fraction IV which would correspond to Fischer's solid bitumen. In explaining this, Broche and Bahr suggested that the difference might lie in the particle size of the inert material. If the granules were too small, they said, the pores and capillaries would be too few and small to hold the added extract firmly. Hence, the extract distilled away from the mixture before any binding action could be exerted. This argument could be used better against Fischer's work than Bone's, since Bone used a 10-gram sample (supporting a 100-gram weight) in a cylinder which was heated in an oven, whereas Fischer used only 1.5 grams in a crucible over a burner. The experiments of Lierg²⁶⁸ indicated that the well-fused coke obtained by Fischer was caused by very rapid heating of the

²⁶¹ Gryaznov, N. S., *Khim. Tverdogo Topliva*, **7**, 533-44 (1936); *Chem. Abs.*, **31**, 2777 (1937).

²⁶² Duparque, A., and Massinon, J., *Ann. mines Belg.*, **39**, 271-342 (1938); *Chimie & industrie*, **42**, 36 (1938).

²⁶³ Dolch, M., *Brennstoff-Chem.*, **7**, 199-203 (1926).

²⁶⁴ Van der Waerden, J., *Fuel*, **6**, 252-6 (1927).

²⁶⁵ Davis, J. D., and Reynolds, D. A., *Ind. Eng. Chem.*, **18**, 838-41 (1926), **21**, 1295-8 (1929); *Fuel*, **5**, 405-11 (1926).

²⁶⁶ Broche, H., and Bahr, T., *Brennstoff-Chem.*, **6**, 349-54 (1925).

²⁶⁷ See p. 175 of ref. 124.

²⁶⁸ Lierg, F., *Z. angew. Chem.*, **35**, 264-8 (1922).

samples, and Hall²⁶⁹ pointed out that an extracted coal cannot be considered a suitable inert material because of its large adsorptive capacity. Mühlsteph²⁷⁰ extracted the same coal as Fischer and from the analyses reported little difference in the samples, yet rather large differences in yield and amount of oily bitumens (Table XLVIII) were obtained by the two work-

TABLE XLVIII

YIELD OF EXTRACT FROM OSTERFELD COAL²⁷⁰

	Volatile Matter	Fixed Carbon	Percent Bitumens		
			Total	Oily	Solid
Fischer	17.14	82.86	3.15	0.98	2.17
Mühlsteph	19.9	80.1	6.8	3.88	2.92

ers. He further reported data which showed no relationship between the oily bitumen content of a coal and its caking index.

A relationship²⁷¹ has been reported, however, between the reactivity of cokes and the oily bitumen content of the original coal, and it has further been shown that the reactivity of cokes prepared from extracted coal is greater than that of cokes prepared from the bitumen.²⁷²

Agde and von Lynckner²⁷³ made extractions with benzene on a series of German coals (Fischer's method) and tried to reconcile the conflicting theories of Bone and Fischer. Coking tests were conducted by both procedures. The conclusions, which, they carefully pointed out, applied only to

their own experimental conditions, were briefly as follows:

1. The bitumens of a coal are not completely removed by extraction with benzene under pressure, whatever that means.

2. The oily bitumens are the caking, and the solid bitumens are the swelling agents only under certain conditions. The importance of the oily fraction lies chiefly in the fact that it reduces the melting point of the total bitumen contained in the coal, and in the first stages of carbonization it forms a solvent for the solid bitumen.

3. Fine grinding of coal increases the caking capacity but reduces the amount of swelling.

4. Rapid heating increases the caking capacity of bitumens because it leads to greater tar formation.

5. The caking properties of a coal cannot be restored by reunion of the separate extraction products since the special form of the bitumens in the original coal (colloidal or gel structure) has been destroyed.

6. The reasons given for the failure of Bone and Davis and Reynolds to confirm the results of Fischer, particularly with respect to the swelling capacity of the solid bitumens, were: (a) insufficient quantity of bitumen; (b) unsuitable concentration of the bitumen solution; (c) unsuitable particle size of the diluent; (d) too low rate of heating; (e) abnormal experimental conditions, i.e., carbonization under pressure, etc.

7. The caking capacity of a coal is essentially determined by chemical processes, i.e., by the course of decomposition of the bitumens. The greater the quantity of the nondistilling solid decomposition product tar formers, the greater is the possibility of obtaining a good coke (Novak and Hubáček¹¹² and Berl and Koerber²⁵³). The physical configuration of the coal residue and particularly its capillarity are of great

²⁶⁹ Hall, P. E., *J. Chem. Met. Mining Soc., S. Africa*, **30**, 195-219 (1930); *Chem. Abs.*, **24**, 3198 (1930).

²⁷⁰ Mühlsteph, W., *Brennstoff-Chem.*, **10**, 241-7 (1929).

²⁷¹ Mezger, R., and Pistor, F., *Teer*, **24**, 569-72, 586-9, 603-6 (1926); *Gas- u. Wasserfach*, **69**, 1061-6 (1926).

²⁷² Agde, G., and von Lynckner, L., *ibid.*, **70**, 1016-9 (1927).

²⁷³ Agde, G., and von Lynckner, L., *Die Vorgänge bei der Stückkohlebildung*, W. Knapp, Halle (Saale), 1930, 24 pp.

importance in determining the caking capacity.

8. The swelling process of the coal is probably determined by physical qualities, i.e., the plasticity and gas permeability of the coal flux. In this respect the ratio of bitumen to coal residue is important in that it affects the permeability of the mass.

Crussard²⁷⁴ has made a distinction between impregnation and mere mixing in reproducing a coal from its extraction products. This author believed that the most active agglutinants were the asphaltenes (corresponding to solid bitumens). Lierg's²⁶⁸ law, "When bituminous substances of the same origin are arranged in a series of decreasing solubility, they are arranged in a series of increased agglutinating power," was quoted, and an application was made to the work of Bone on this basis.

A number of other papers also deal with the interesting and controversial subject of the relationship between coking and the product obtained in extraction.²⁷⁵

²⁷⁴ Crussard, L., *Fuel*, **9**, 177-91 (1930).

²⁷⁵ Boudouard, O., *Compt. rend.*, **148**, 348-51 (1909). Bone, W. A., Pearson, A. R., Sinkinson, E., and Stockings, W. E., *Proc. Roy. Soc. (London)*, **100A**, 582-98 (1921). Lategan, P. N., *S. African J. Ind.*, **6**, 609-16 (1923); **7**, 41, 103-8 (1924). Bone, W. A., *J. Soc. Chem. Ind.*, **44**, 291-9T (1925). Mayer, E., *Braunkohlenarch.*, No. 18, 1-58 (1927). Hankiss, S., *Szénkísérleti Közlemények*, **2**, 57, 67-70 (1927); *Chem. Zentr.*, **1929**, II, 677. Tawada, K., *J. Fuel Soc., Japan*, **7**, 41-7 (1928); *Chem. Abs.*, **22**, 3278 (1928). Lambris, G., *Brennstoff-Chem.*, **12**, 181-7 (1931). Connerade, E., and Meunier, C., *Chimie & industrie*, **1931**, Spec. No., 267-86. Mendelsohn, J., *J. S. African Chem. Inst.*, **15**, 46-53 (1932); *Chem. Abs.*, **26**, 6097 (1932). Tulparoff, A. I.,

In addition to the literature already cited a number of publications have appeared from time to time which have been entirely or largely surveys in nature.²⁷⁶ Of these the most thorough articles are those of Kester, Stopes and Wheeler, and Bakes.

Khim. Tverdogo Topliva, **3**, 378-80 (1932); *Chem. Abs.*, **28**, 5966 (1934); *Coke and Chemistry (U.S.S.R.)*, **9**, 53-6 (1933); *Chem. Abs.*, **29**, 7043 (1935). Peters, K., and Cremer, W., *Brennstoff-Chem.*, **14**, 445-50 (1933). Blom, I. J. B., *J. Chem. Met. Mining Soc. S. Africa*, **34**, 1-44 (1933). Chorazy, M., *Fuel*, **13**, 294-9 (1934). Rossow, O., *Braunkohlenarch.*, No. 51, 3-32 (1939).

²⁷⁶ Muck, F., *Grundzüge und Ziele der Steinkohlen Chemie*, Strauss, Bonn, 1881, 170 pp. Bell, I. L., *Rept. Brit. Assoc. Advancement Sci.*, 1894, pp. 246. Hodurek, R., *Oesterr. Chem.-Ztg.*, **7**, 365-70 (1904). Wibaut, J. P., *Chem. Weekblad*, **12**, 758-65 (1915). Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, **1**, 43-53 (1916). Fischer, F., and Gluud, W., *Glückauf*, **52**, 721-9 (1916). Anon., *J. Soc. Chem. Ind.*, **35**, 1136-7 (1916). Fischer, F., *Ges. Abhandl. Kenntnis Kohle*, **2**, 1-27 (1917), **3**, 246-7 (1919), **5**, 658-92 (1920); *Brennstoff-Chem.*, **1**, 31-9 (1920). Stopes, M. C., and Wheeler, R. V., *Fuel*, **3**, 3-11, 63-7, 97-105, 129-33, 179-84, 196-204, 254-61, 288-97, 328-35, 356-60, 393-9, 439-52 (1924). Fischer, F., and Lessing, R., *Conversion of Coal into Oils*, E. Benn, London, 1925, 284 pp. Fieldner, A. C., and Davis, J. D., *Trans. Am. Inst. Mining Met. Engrs.*, **71**, 227-45 (1925). Quarendon, R., *J. Soc. Chem. Ind.*, **45**, 468-70 (1926). Shohan, J. B., *U. S. Bur. Mines, Circ.* **6212** (1929), pp. 14. Kester, E. B., *Fuel*, **10**, 277-85 (1931). Lessing, R., *Gas World*, **96**, 331-3 (1932); *Gas J.*, **197**, 791-3 (1932). Bakes, W. E., *Dept. Sci. Ind. Research (Brit.)*, *Fuel Research, Tech. Paper* **37** (1933), pp. 214. Crookall, R., *Naturalist*, August, 1933, pp. 169-76; *Rev. Geol.*, **14**, 491 (1935). Moehrle, E., *Angew. Chem.*, **48**, 509-13 (1935). McCulloch, A., *J. Soc. Chem. Ind.*, **54**, 997-1004 (1935). Ref. 195. Lowry, H. H., *J. Inst. Fuel*, **10**, 291-301 (1937). Titov, N. G., and Fedoseeva, S. F., *Khim. Tverdogo Topliva*, **8**, 793-803 (1937); *Chem. Abs.*, **32**, 2324 (1938). Scheer, W., *Feuerungstechn.*, **27**, 225-30 (1939).

CHAPTER 20

VACUUM DISTILLATION OF COAL

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All investigations of the action of heat on coal in vacuum have shown that, except for small amounts of water vapor, oxides of carbon, and low-molecular-weight hydrocarbons, no distillation occurs until such temperatures are reached that there is definite evidence of thermal decomposition. Thus, "vacuum distillation of coal" is, in reality, thermal decomposition at reduced pressure accompanied by distillation of the thermal degradation products. A complicating factor in the application of heat to coal, in a highly evacuated system, arises from the fact that, as temperatures are reached at which distillation of molecules of moderate weight, if present, would be expected to take place, or at which primary degradation products could be split out and vaporized, other reactions involving condensation to larger molecules or to more completely linked network structures, by loss of water, hydrogen, or methane, are also taking place rapidly. Since reduction in pressure accelerates these condensation reactions, competition by the condensation processes is responsible for the very limited yields of degradation products of moderate molecular weight obtained by thermal decomposition in vacuum, especially at low heating rates. The failure of bituminous coals to furnish any significant amounts of distillate, even in a molecular still, at temperatures below those at which decomposi-

tion starts, shows that they are either net-like polymeric structures, in which all the atoms of a given fragment are connected by primary bonds, or if they are mixtures of molecules all but an insignificant fraction of the component molecules are of such size as to preclude evaporation. Since the largest molecule¹ which can be distilled has a molecular weight of less than 1,000, an approximate lower limit is set for the size of the molecules which can be present in coal.

The early work of Burgess and Wheeler² in this field was concerned only with the amounts and nature of the gaseous products formed. Evacuation and collection of gases were carried out by a Sprengel pump, and, since the still and the pump were connected with small-bore tubing, it is likely that the actual pressures at the surface of the decomposing coal corresponded to several centimeters of mercury. The chief conclusion reached was that, since the paraffin hydrocarbons form by far the greatest fraction of initial gaseous decomposition products, either just above or below the

¹ Carothers, W. H., and coworkers, *J. Am. Chem. Soc.*, **52**, 5279-88 (1930); especially p. 5284. Burch, C. R., *Proc. Roy. Soc. (London)*, **A123**, 271-84 (1929).

² Burgess, M. J., and Wheeler, R. V., *J. Chem. Soc.*, **97**, 1917-35 (1910), **99**, 649-67 (1911). Clark, A. H., and Wheeler, R. V., *ibid.*, **103**, 1704-22 (1913).

"critical temperature," coal contains two types of compounds of different degrees of stability, the least stable yielding paraffin hydrocarbons and no hydrogen, and the more stable yielding hydrogen alone. The difference in yields of hydrocarbons and of hydrogen for the different coals was ascribed to the "different proportions of paraffin- and hydrogen-yielding constituents" present in them. It was also shown that among different bituminous coals very different proportions of the "volatile matter" might appear as paraffin hydrocarbons, for bituminous coals of 40.6, 35.5, 33.07, and 30.1 percent volatile matter yielded respectively 47.9, 53.3, 62.7, and 47.2 cubic centimeters of paraffin hydrocarbons per gram of dry, ash-free coal when heated up to 650° C in vacuum.

The nature of the liquid products formed by decomposition of coal in vacuum was studied by Pictet and Ramseyer,³ who in their first work distilled 1.75 kilograms of Montrambert bituminous coal in 250-gram portions in an iron tube, which was evacuated to 10 millimeters mercury pressure by a water aspirator. The temperature was not measured exactly but was said not to have risen above 450° C. Sixty grams, 3.5 percent, of a liquid distillate were obtained. Fractionation at ordinary pressures resulted in collection of liquids between 150 and 350° C, the physical and chemical properties of which indicated hydroaromatic molecules. Aromatic hydrocarbons and phenols were absent. A fraction collected between 255 and 285° C corresponded to hexahydrofluorene.

In a continuation of earlier work, Wheeler⁴ and coworkers studied the de-

composition of a number of English bituminous coals. Two-hundred-gram samples were heated in a round, Jena glass retort (Fig. 1). The original evacuation was by means of a Geryk oil pump, and a Sprengel pump was used for gas collection as before. It was found that, when a coal, Silkstone,

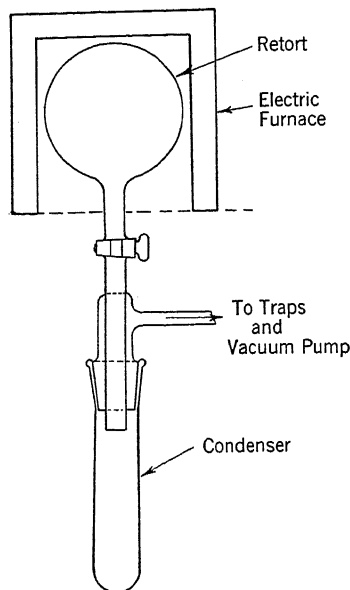


FIG. 1. Retort for vacuum distillation of coal.⁴

which had been finely ground and dried in air at 107° C was evacuated at room temperature, oxides of carbon were the chief gases removed, whereas, from "newly won" undried coal, hydrocarbons predominated. Gases continued to appear in small amounts up to 200° C. At this temperature there was copious evolution of water along with oxides of carbon. In the range 200 to 300° C, sulfur-containing gases appeared along with higher olefines. Liquids other than water began to distil at 310° C, and at 350° C there was rapid gas evolution and much viscous oil. Later,⁴ a larger still was employed—1.25 kilograms of coal

³ Pictet, A., and Ramseyer, L., *Ber.*, **44**, 2486-97 (1911).

⁴ Burgess, M. J., and Wheeler, R. V., *J. Chem. Soc.*, **105**, 131-40 (1914). Jones, D. T., and Wheeler, R. V., *ibid.*, **105**, 140-51 (1914).

could be treated at one time—and sufficient liquid products were collected to permit examination. The vacuum was stated to be 5 to 40 millimeters of mercury. The results with Scottish, 26.36 percent volatile matter, and with Durham, 30.81 percent volatile matter, bituminous coals, were as follows: at temperatures up to 430° C, 6.5 percent by weight of the coal was recovered as tar, which, on distillation to 300° C, yielded 50 percent pitchy residue. The distillate was 40 to 45 percent unsaturated hydrocarbons, richer in carbon than C_nH_{2n} ; 40 percent liquid paraffins and naphthenes; 12 to 15 percent phenolic bodies, chiefly cresols and xylenols; 7 percent aromatics, chiefly naphthalene homologs, and solid paraffins. Pyridine bases were found in traces only. The presence of hydrochloric acid and of ammonium chloride was reported in the liquor. These results differ from Pictet's in showing the presence of both phenols and aromatic hydrocarbons. Later work^{5, 6} has indicated that the phenols are largely produced by secondary decomposition, and it seems probable that secondary decomposition did take place in Wheeler's work in view of the large mass of coal employed and the relatively unfavorable conditions for evaporation and removal from the system of the primary products.

Porter and Taylor⁷ studied the decomposition of four typical American bituminous coals in a vacuum ranging from 0.5 to 10.0 millimeters at 50° temperature intervals up to 450° C. Fifteen-gram samples of 40- to 100-mesh coal were used in the lower-temperature experiments and 5-gram

samples in the higher. The decomposition was carried out in a glass bulb immersed in a constant-temperature bath of mixed sodium and potassium nitrates. The coals studied ranged from high-rank bituminous to subbituminous—Pocahontas, Pittsburgh, Illinois, and Wyoming.

It was concluded that neither the course of the decomposition nor the temperature at which it began was materially affected by a reduction in pressure. The abrupt increase in rate of hydrogen evolution which was found to occur above 700° C was ascribed to "secondary" decomposition of volatile matter rather than to any characteristic change in the decomposition of the main coal substance. Two types of decomposition were recognized: one in which water, carbon dioxide, and carbon monoxide were expelled; and another producing liquid and gaseous paraffin hydrocarbons, the type of decomposition product predominating below 500° C, depending upon the coal. In the subbituminous Wyoming coal, the reaction producing water, carbon dioxide, and carbon monoxide was found to predominate up to 450°. The high yields of tar obtained from all the coals by distillation up to 450°, as compared with those in high-temperature distillation, were emphasized.

Pictet and coworkers⁸ in an important series of investigations continued their work on decomposition of Montrambert coal on a larger scale, using a gas-heated, cast-iron retort, 60 centimeters high and 20 centimeters in diameter. Temperatures of 450 to 500° C were used. The vacuum system was not described, but the pressure was stated to be 15 to 17 millimeters of mercury. By distillation for 5 hours at 450° C, 1.5 per-

⁵ Juettner, B., and Howard, H. C., *Carnegie Inst. Tech., Coal Research Lab. Contrib.* 8 (1934), 22 pp.

⁶ Juettner, B., and Howard, H. C., *Ind. Eng. Chem.*, **26**, 1115-8 (1934).

⁷ Porter, H. C., and Taylor, G. B., *Proc. Am. Gas Inst.*, **9** (1), 234-88 (1914).

⁸ Pictet, A., and Bouvier, M., *Compt. rend.*, **157**, 779-81, 1436-9 (1913), **160**, 629-31 (1915); *Ber.*, **46**, 3342-53 (1913), **48**, 926-33 (1915); *Chem.-Ztg.*, **38**, 1025 (1914).

cent of liquor and 4 percent of tar were recovered, the general composition of which was: 30 percent saturated hydrocarbons, 68 percent unsaturated hydrocarbons, and 2 percent alcohols. Bases were reported in small amounts. The saturated and unsaturated hydrocarbons were separated with liquid sulfur dioxide. The hydrocarbons, alcohols, and bases were examined in detail. From the material insoluble in sulfur dioxide, hydrocarbons of the general composition C_nH_{2n} , ranging from C_9H_{18} to $C_{30}H_{60}$, were isolated in a pure state. A hydrocarbon of the composition C_6H_{12} had the properties of hexahydromesitylene, and one of $C_{10}H_{20}$, those of hexahydrindene. The hydrocarbon $C_{30}H_{60}$ was believed to be identical with melene. From the material soluble in sulfur dioxide, the following hydrocarbons were isolated: dihydro-*m*-xylene, dihydromesitylene, three compounds having the formula $C_{11}H_{16}$ and having three double bonds each, but not definitely characterized, and hexahydrofluorene. The cyclic alcohols were recovered by reaction with sodium, and compounds of the following composition were reported: $C_7H_{14}O$, which was a hexahydrocresol, and four of the general composition $C_nH_{2n-6}O$, where n ranged from 8 to 11, which were not more closely characterized. A mixture of toluidins, C_7H_9N , was separated as well as a number of bases of the following compositions: C_8H_7N , C_9H_9N , $C_{10}H_{11}N$, and $C_{12}H_{15}N$, all of which formed crystalline picrates and possessed a quinoline odor but could not be definitely characterized.

The preponderant amount of alkylated structures reported is noteworthy and is characteristic of the low-temperature distillation products of coal, whether the decomposition is carried out in vacuum or at ordinary pressures. These workers pointed out that the physical constants of the C_nH_{2n} series of hydrocarbons obtained in their vacuum distillation bore great simi-

larity to those of hydrocarbons isolated from Galician and California petroleum by Mabery.

Schneider and Tropsch⁹ reported on the distillation of brown coal in vacuum. From 100 to 150 grams of "hazelnut"-size brown coal was heated in an iron cylindrical retort 16.5 centimeters high and 7 centimeters in diameter. Evacuation was by means of a Gaede oil pump, but, because of the small-bore connecting tubing and the series of traps employed, it is uncertain what the pressure was in the retort. It was stated that because of gas evolution, resulting from decomposition, a high vacuum could not be maintained. Under these conditions it was not found possible to distill the "bitumens" of the brown coal without decomposition. In contrast to results of distillation of this type of coal at ordinary pressures, the vacuum distillation was stated to give a good yield of "viscous oil."

Burgess and Wheeler¹⁰ later continued their examination of the gaseous products formed by decomposition of bituminous coals in vacuum. The products obtained by treating a Lancashire coking coal by the same procedure as applied to the Silkstone coal, at various temperature intervals, are indicated in Table I. The sample which was essentially "clarain" was "newly won" and undried. In the 200 to 300° C stage most of the gas appeared between 270 and 300° C, and a reddish brown oil, together with considerable water, distilled at 280° C. The temperature 270 to 280° C was regarded as the initial decomposition temperature of this coal, for, "apart from the distillation of oil, the composition of the gases, in particular the high content of oxides of carbon, differentiates them from the

⁹ Schneider, W., and Tropsch, H., *Ges. Abhandl. Kenntnis Kohle*, **2**, 28-35 (1917).

¹⁰ Burgess, M. J., and Wheeler, R. V., *Fuel*, **5**, 65-8 (1926).

TABLE I
DECOMPOSITION OF LANCASHIRE COKING
COAL * IN VACUUM ¹⁰

Temperature °C	Time hours	Cubic Centimeters of Gas per 100 Grams of Coal				Higher Hydro- carbons
		CO	CO ₂	H ₂	CH ₄	
Room tem- perature	369	2.2	3.0	104
25-100	96	3.8	6.0	118
100-200	24	1.2	2.6	0.2	10	16
200-300	36	1.8	10	0.3	0.8	6.8
300-400		29	210	175	617 †	

*Volatile matter, 30.85%; fixed carbon, 62.45%; ash, 4.9%.

† Methane plus higher hydrocarbons.

occluded gases obtained at lower temperatures." In connection with this statement it should be noted that whereas the percentage of oxides of carbon in the gases obtained in the temperature range indicated is very much higher, there is little difference in the mass of oxides of carbon per gram of coal, between the gases evolved at room temperature and those in the 200 to 300° C range. There is, however, very dis-

tinct evidence of decomposition in the 300 to 400° C stage, both from the standpoint of the mass of oxides of carbon and the mass of hydrogen evolved.

In a later paper ¹¹ a similar experimental technique was applied to typical British bituminous coals. The results and conclusions from experiments on a sample of "bright" coal from the "Wigan 6-foot seam" may be summarized as follows: coal has a definite decomposition point not appreciably affected by experimental conditions; with this coal it is 318° C and a month's heating in vacuum at 310° C caused no appreciable decomposition. Characteristic products of the decomposition were found to be water and phenolic compounds and gaseous paraffins. As soon as the decomposition point of the coal was passed, its characteristics, as evinced by its behavior toward solvents, its caking powers, and its reactivity in general, underwent a sudden and marked change. The hydrocarbons and resins, ex-

¹¹ Holroyd, R., and Wheeler, R. V., *J. Chem. Soc.*, 1928, 2669-77, 3197-3203.

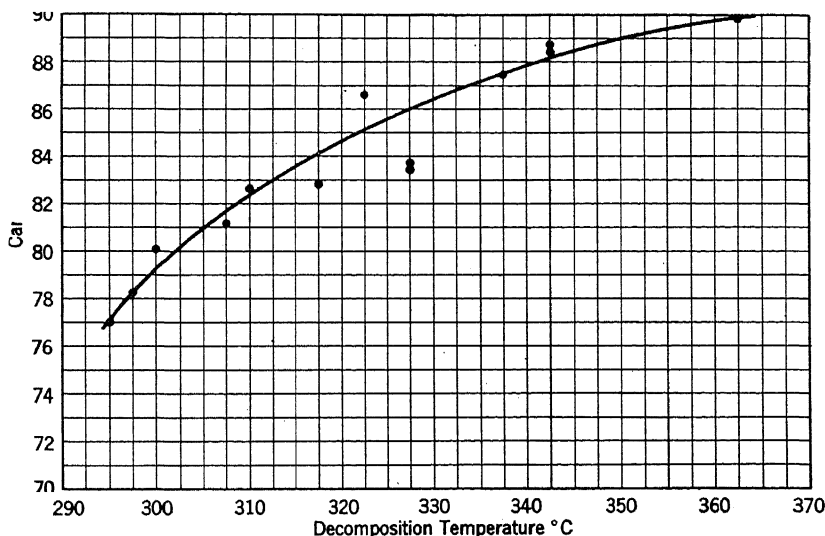


FIG. 2. Relation between carbon content and decomposition temperature.¹¹

tractible from the coal by organic solvents, were found to be responsible for a high proportion of the oils obtained on distillation. The temperatures of active decomposition were found to vary for different bituminous coals, and the data given indicate a definite correlation between carbon content and temperature of decomposition, Fig. 2. The rates of formation of gaseous paraffin hydrocarbons, phenolic bodies, and water through the critical range for the Wigan coal are shown in Fig. 3.

Stone and Travers¹² have carried out a thermal decomposition of a British bitu-

¹² Stone, V., and Travers, M. W., *J. Soc. Chem. Ind.*, **52**, 686-7 (1933).

minous coal in a glass still evacuated by a combination of mercury vapor and mechanical pumps. Although this design (Fig. 4) is undoubtedly much superior to any previously described, it seems probable that pressures inside the still were considerably higher than those measured by the gage near the pump, and reported at 10^{-2} millimeter of mercury, and hence that the requirements for molecular distillation were not fulfilled.

The data obtained are given in Table II. The experiments indicated that the quantity of distillate increased rather rapidly above 350°C . Reduction of particle size

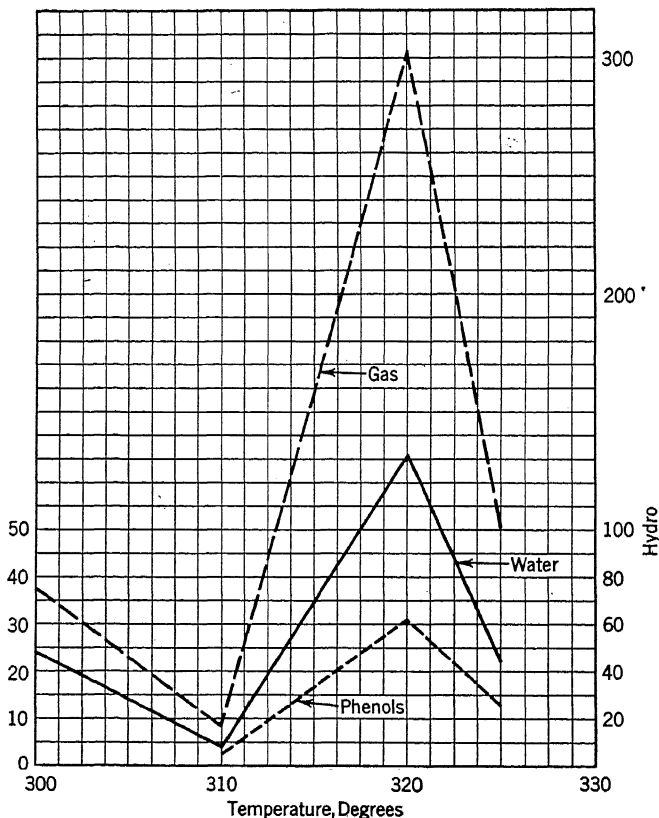


FIG. 3. Rates of formation of gaseous hydrocarbons, water, and phenols through the critical range.¹¹

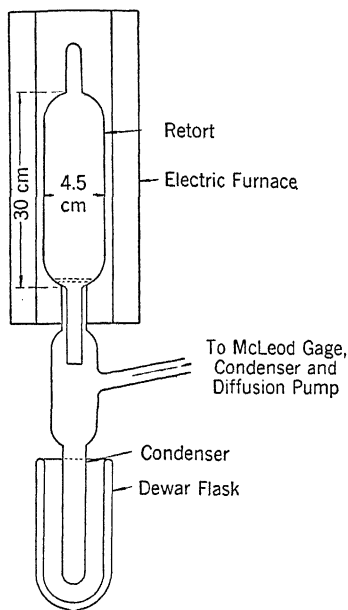
FIG. 4. Vacuum distillation apparatus.¹²

TABLE II

DECOMPOSITION OF STAVELEY COAL * IN VACUUM¹²

Weight of coal, grams	229.3	218.1	26.72	218.0
Temperature, °C	350	350	350	365
Time, days	6	6	5	1
Coal size, inches	1/10	1/60	1/120	1/10
Loss in weight, percent	9.4	10.6	10.7	13.2
Average pressure, centimeters of mercury			10 ⁻³	10 ⁻⁴

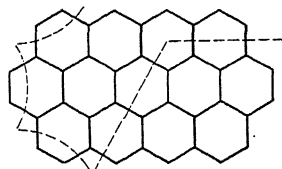
DISTILLATE, WEIGHT PERCENT OF COAL

Benzene-soluble	5.16	4.87	6.84
Alcohol-soluble	0.43	0.13	2.70
Liquid hydrocarbons	1.52	2.29	
Water	1.05	1.37	
Gas and loss	1.22	2.15	

* Volatile matter, 36.8% ; fixed carbon, 54.8% ; ash, 5.7%.

to $\frac{1}{120}$ inch seemed to have little effect. The greater part of the condensate was collected during the first 2 or 3 days, but the process had not actually come to an end in 5 or 6 days. The yield of distillate at 350° C approached the quantity of product

obtained by benzene pressure extraction. The process, even at 350°, was believed to involve chemical decomposition as evidenced by gas formation. An interesting picture of the possible mechanism of the process was outlined as follows: "If one assumes that coal consists of very large molecules of continuous hexamethylene structure, one may imagine that decomposition by distillation involves the migration of hydrogen atoms toward the edge of the structure and the subsequent breaking away of hydrocarbon molecules ranging from gases to tars." It is easy to see how this takes place, without the formation of hydrocarbons of intermediate molecular weight in any large quantity, if one regards the decomposition of coal as taking place as indicated in Fig. 5. The change shown is

FIG. 5. Thermal decomposition of condensed cyclic structures.¹³

analogous to that taking place when tetrahydronaphthalene breaks down.¹³

Juettner and Howard^{5,6} have studied the decomposition of a Pittsburgh Seam coal in a still which was designed to provide the most favorable conditions for the decomposition of coal in vacuum, that is, elimination of collisions in the gas phase or with surfaces of higher temperature than those at which the volatile products originated. The importance of the maintenance of a low pressure in such a system is obvious when it is considered that, while the mean free path of a hydrocarbon molecule such as methane, at 350° C, is only changed

¹³ Travers, M. W., *J. Inst. Fuel*, **6**, 253 (1932-33).

about a hundredfold when the pressure is reduced from 1 atmosphere to 10 millimeters of mercury, it is increased ten thousandfold when the pressure is further re-

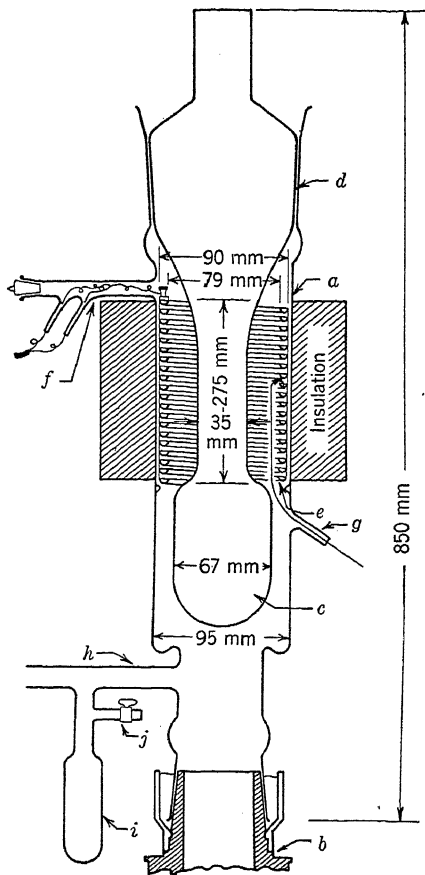


FIG. 6. Molecular still.^a

duced from 10 millimeters to a thousandth of a millimeter of mercury. The apparatus is shown in Fig. 6. The still, of Pyrex glass, rested directly on the mouth of a Gaede four-stage mercury diffusion pump which was in turn backed by a high-speed oil pump. The diffusion pump had a speed of 18 to 20 liters per second at pressures

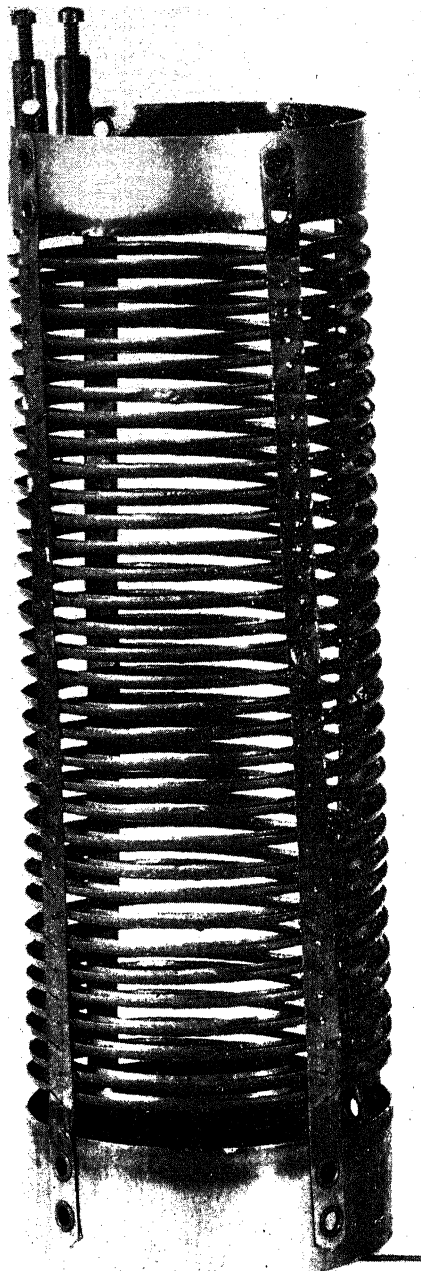


FIG. 7. Coal holder and heater.^a

of 10^{-3} millimeter of mercury and delivered the gases to the oil pump at backing pressures as high as 15 millimeters of mercury. The coal holder, shown in Fig. 7, consisted of a helix of light-gage nickel 0.5-millimeter wall, the individual turns of which were

on the walls, the whole middle section of the still was well insulated.

The effects of temperature and of heating rate are illustrated in Fig. 8. Curve 1 shows the yield of condensate obtained at different temperatures in a continuous step-

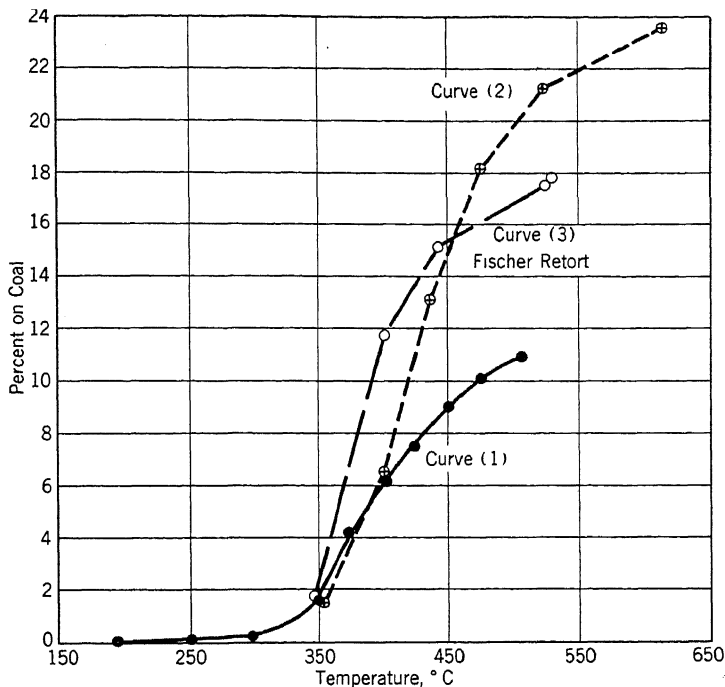


FIG. 8. Effect of heating rate.⁶

semicircular in section, mounted concave side up on a mica support. The coal, of which approximately 50 grams could be used, was placed in the trough thus formed. The coal holder was heated internally by an electric current, carried by flexible leads which passed through the still wall in large copper-to-glass seals. The temperature of the heater was determined and controlled by a thermocouple junction silver-soldered to the inside of the trough in which the coal lay, near the center of the helix. To avoid condensation of high-boiling products

wise distillation of the same sample, 108 hours being required to reach the maximum temperature. The marked effect of heating rate on yield of condensate is evident by comparison with curve 2, where the coal was heated in approximately 1 hour to the various distillation temperatures indicated and maintained at the distillation temperature for 6 hours.

Gaseous products were not collected in these experiments, but, since the rate of pumping was constant, pressure readings in the system furnish an index of gas evolu-

tion. From Fig. 9, it is apparent that gas evolution starts at a temperature before appreciable amounts of condensable products are evolved and continues as long as such products are obtained. Hence, it seems improbable that any significant frac-

this effect is due to the "solvent action" of the initial decomposition products of the coal upon the residue, in the distillations in the Fischer retort. In the vacuum distillation the vapor pressure of distilling products at the surface was, except for a short

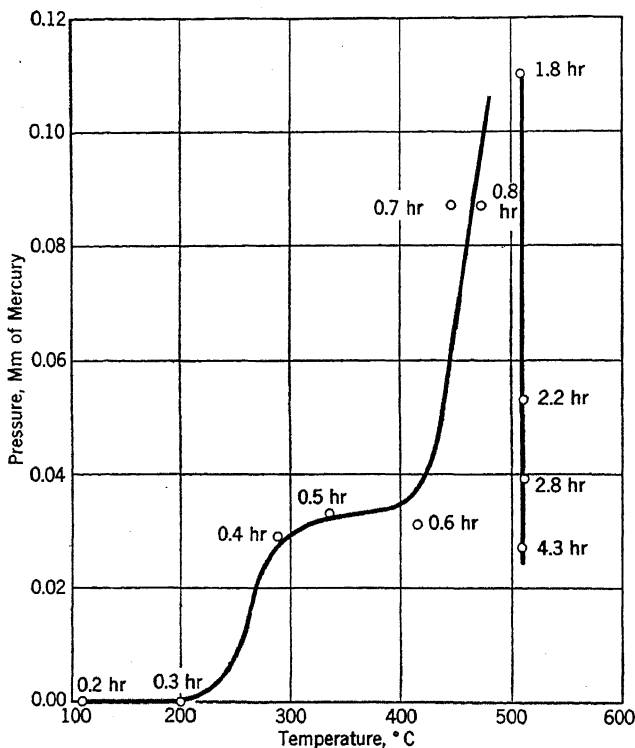


FIG. 9. Rate of gas evolution.*

tion of the substance condensed existed as such in the original coal.

In order to determine the specific effect of reduced pressure on the course of the decomposition, comparative distillations were made in a Fischer retort at atmospheric pressure in nitrogen. The results are shown in curve 3 of Fig. 8. The greatly increased yield at 400° C in the Fischer retort, over that obtained in vacuum at that temperature, is very striking. It is probable that

interval in the distillation, always low, probably less than 0.01 millimeter of mercury, whereas in the Fischer retort it approached 1 atmosphere. Hence, solvent action would be at a minimum in the vacuum distillation.

General material balances for typical vacuum and Fischer retort distillations at 525° C are shown in Table III, and the composition of condensates in Table IV. Because of the polymerizing effect of ele-

TABLE III

GENERAL BALANCES IN VACUUM AND FISCHER RETORT DISTILLATIONS ⁶ AT 525° C

	Vacuum Distillation		Fischer Retort Distillation
	20-40 Mesh	μ -Coal	20-40 Mesh
Coal, grams	100	100	100
Residue, grams	72.2	68.4	76.0
Condensate, grams	21.7	26.0	18.0
Gas, grams	4.8	4.4	5.8

TABLE IV

COMPOSITION OF CONDENSATES ⁶ (20-40 MESH COAL)

	Vacuum Distillation		Fischer Retort Distillation	
	Percent of Condensate	Percent of Coal	Percent of Condensate	Percent of Coal
Neutral { Ether-insoluble	32.24	7.11	15.77	2.78
{ Ether-soluble	40.25	8.61	42.60	7.51
Phenols and acids	11.96	2.56	14.64	2.58
	0.91	0.20	2.3	0.40
Water and loss	10.85	2.32	22.57	3.98

vated temperatures on the primary degradation products of coal, a solvent method of analysis was used for examination of the condensates. They were first separated into material soluble and insoluble in ethyl ether. The material soluble in ethyl ether was then separated into neutral, acidic, and basic constituents in the usual manner. The material insoluble in ethyl ether was essentially neutral, free from "phenols and bases," as indicated by the usual tests, but it undoubtedly contained molecules with phenolic hydroxyls. It is evident from Table IV that the most striking difference between condensates obtained in vacuum and at normal pressures lay in the much greater yield of "neutral ether-insoluble material" in the condensates obtained in the vacuum distillation, and the amount of these materials found in the degradation products of coal appears to be an impor-

tant criterion of the extent to which secondary decomposition had taken place.

An approximately 50 percent greater yield of hydrogen in the vacuum distillation, as compared with that at normal pressures, indicates that this gas is a primary degradation product of the decomposition of this coal at these temperatures. The increase in hydrogen content of the gases with time was the same as is observed in high-temperature carbonization, but the explanation usually offered in that type of decomposition, cracking of methane, is not tenable in vacuum distillation since in that distillation there was no opportunity for extensive secondary decomposition. For this reason, it appears probable that the increasing hydrogen content of the gases with time, in the distillation in vacuum, is due to some change in the mode of the primary decomposition of the coal itself as the distillation proceeds. If the gaseous hydrocarbons formed early in the decomposition are reaction products of hydrogen with aliphatic side chains, then, as these groups are eliminated, the ratio of hydrogen to hydrocarbons must necessarily increase.

The effect of decreased particle size on the nature of the distillate in vacuum is shown in Table V by the increased yield of condensate and especially by the increase in neutral ether-insoluble material and de-

TABLE V

EFFECT OF PARTICLE SIZE ON NATURE OF CONDENSATES ⁶ OBTAINED IN VACUUM DISTILLATION

	$(\mu$ -Coal)	
	Percent of Condensate	Percent of Coal
Neutral { Ether-insoluble	60.0	17.1
{ Ether-soluble	29.0	8.2
Phenols and acids	4.8	1.3
Bases	0.58	0.16
Water and loss	5.62	1.5

VACUUM DISTILLATION OF COAL

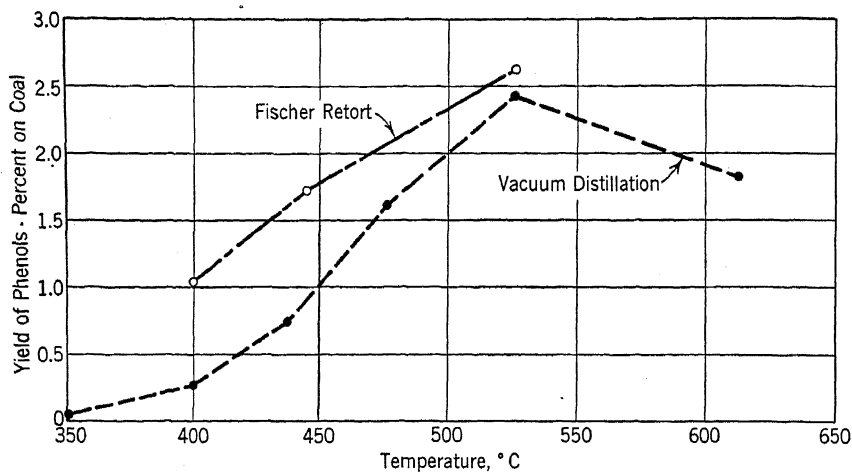


FIG. 10. Yields of phenols in vacuum and at normal pressure.*

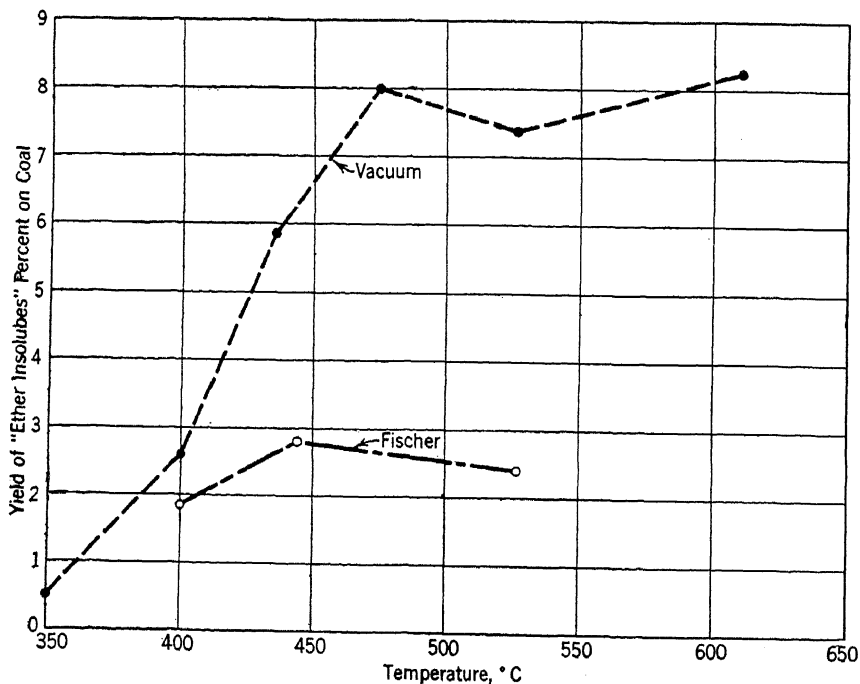


FIG. 11. Yields of neutral ether-insoluble material in vacuum and at normal pressure.*

crease in neutral ether-soluble and phenolic and acidic constituents when coal of particle size of about $1\ \mu$ (0.001 millimeter) was distilled. These results confirm the view that the amount of "neutral ether-insoluble" is a criterion of the extent of secondary decomposition since, the smaller the coal particle, and the shorter the time required for escape of primary products, the higher the yield of neutral ether-insoluble material.

The results of a study of the yields of phenolic and neutral ether-insoluble substances in vacuum and in the Fischer retort, using 20- to 40-mesh coal, are shown in Figs. 10 and 11. The greater yields of neutral ether-insoluble material and lower yields of phenolic bodies obtained in vacuum indicate that the simpler phenolic bodies are produced by decomposition of the neutral ether-insoluble material. This view is confirmed by the low yields of phenols obtained in the vacuum distillation of the insoluble residue from benzene pressure extraction of this coal. The greater part of the phenols formed by decomposition of this coal in vacuum were shown to be derived from the material which was removed by the benzene extraction process.¹⁴

Distillation in vacuum has also been applied to the examination of various macro constituents of coal and to products derived

from it. Jones and Wheeler¹⁵ separated a British bituminous coal into three fractions: (1) insoluble in pyridine, (2) soluble in pyridine, but insoluble in chloroform, and (3) soluble in pyridine and in chloroform. On vacuum distillation, fractions (1) and (2) yielded only small amounts of liquids and these mainly phenols, whereas (3) gave 40 to 50 percent distillate below 400° C and the distillate contained no phenols, but paraffin, olefin, and naphthalene hydrocarbons.

Tideswell and Wheeler¹⁶ applied decomposition in vacuum along with solvent extraction, and the action of certain reagents to samples of banded constituents of a British bituminous coal. Their findings are of broad interest.

The general impression created . . . is of a gradation of properties as we pass from vitrain to durain. Fusain stands apart. No characteristic reaction or behavior for any one of the components of banded coal, such as might be expected were there a fundamental difference in chemical composition, was disclosed. Whilst making clear interesting differences . . . the work has not revealed the presence of essentially distinct types of chemical compounds peculiar to any of the ingredients of banded coal.

¹⁵ Jones, D. T., and Wheeler, R. V., *J. Chem. Soc.*, **107**, 1318-24 (1915). For a general review see Wheeler, R. V., *J. Inst. Fuel*, **12**, 8-19 (1938).

¹⁶ Tideswell, F. V., and Wheeler, R. V., *J. Chem. Soc.*, **115**, 619-36 (1919).

¹⁴ Unpublished data, Coal Research Laboratory.

INDUSTRIAL COAL CARBONIZATION

FRED DENIG

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Industrial coal carbonization is carried on in America in large-scale operations either as beehive or as byproduct coking. The characteristic feature of beehive coking is the production of the necessary heat by combustion within the oven. In byproduct coking, on the other hand, the production of the heat necessary for coking is in flues adjacent to the chamber holding the coal, the heat passing through the wall that separates the coal-containing chamber and the flues. No air is permitted to enter the byproduct oven, and all volatile byproducts are withdrawn from the chamber and collected within a "collecting main" for transmission to the byproduct house where they are separated from the gas in either the gaseous, liquid, or solid phase by scrubbing, cooling, chemical reactions, or other methods. The byproduct oven is usually a narrow, high, and relatively long chamber; groups built adjacent to one another are known as batteries. The ovens hold from 5 to 30 tons of coal, the average American oven holding from 12 to 18 tons of coal, depending upon its dimensions. Such ovens are charged from their tops, provided with end doors, which are removed when coking is complete and the coke is pushed out horizontally with a ram on a machine called a pusher.

Small-scale operations include a variety of designs of retorts. Almost all types of intermittent retorts are byproduct ovens. In the intermittent ovens the charge is static. The oven may be a small circular or D-shaped section of various lengths usually holding only a few hundred pounds of coal; or it may be built on an angle so that the resultant coke can slide out by its own weight when the door is removed; or the chamber may be vertical and the resultant coke dropped out by means of a bottom door; or the oven may be a small reproduction of the larger oven designs. Continuous retorts allow the coal to move downward through a high, narrow, vertical chamber. Heating is carried on as in other types of byproduct systems, and byproducts are removed and collected. Sole-heated ovens are a form of byproduct oven wherein the heating flues are located below the oven floor and the heat passes through the floor to reach the coke. In electrically heated ovens, the heat developed by passing electricity through a layer or core of coke adjacent to or within the coal mass is used for coking the charge. In all the systems cited above the resultant coke is heated up to a temperature ranging from 1,500 to 2,000° F (average practice 1,700 to 1,900° F). In low-temperature carbonization the temperature of the end product,

i.e., the coke, is held to not over 1,000° F. Mid-temperature coking, which involves the coking of special mixes at intermediate end temperatures of 1,200 to 1,300° F, is entirely European and has never been tried in America.

Almost the entire American coke production since 1935 has been carried on in the horizontal chamber byproduct coke oven. The production of beehive coke has been so small during the greater part of the period 1930 to 1940 as to be almost negligible. Beehive coke ovens are now considered only standby carbonization equipment of low capital cost to take up excess demand that might arise during periods of extraordinary industrial activity caused by short boom times or by war. Only a few remaining continuous and intermittent vertical retorts are in operation. These retorts as well as the old horizontal and inclined retorts have been almost entirely displaced by the large central byproduct coke plants for gas- and coke-making purposes. These large central carbonization works are located at strategic centers with consideration to shipment and delivery of coal, use or marketing of coke, and distribution of gas. Another factor contributing to the obsolescence of the small vertical and horizontal retorts has been the appearance and delivery of natural gas in the entire Mississippi Valley area, lower Pacific Coast area, Rocky Mountain areas, etc. This fact has eliminated hundreds of small coal-gas manufacturing plants. The large central works on the Atlantic Coast have hastened the elimination of the small plants in that area. Low-temperature carbonization has never in the past proved of much interest or value to the American carbonization industry. It is doubtful that true low-temperature coke has any future in the American fuel market, although it may be of great value in Mexico and Latin America as a

substitute for wood charcoal for domestic purposes. Low-temperature char promises to have value as a substitute for low-volatile coal where coals are blended and the cost of low-volatile coal is too great to justify its use. This is particularly true of the Rocky Mountain, Pittsburgh, and southern coking areas.

THE BEEHIVE OVEN

The beehive oven is the oldest form of oven used for carbonizing coal. In the

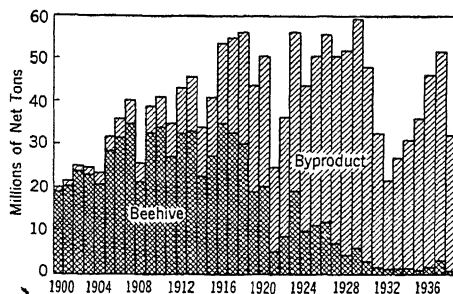


FIG. 1. Production of beehive and byproduct coke in the United States, 1900-38.¹

year 1916 as much as 120,000 tons of coal per day were carbonized in the beehive oven; during the great depression this figure fell to less than 1,000 tons per day; in January, 1941, this figure increased to 19,000 tons per day. The trend in production of coke by these two methods is shown in Fig. 1.¹ For many years some beehive ovens will still be operated; they do offer a means of manufacturing coke at low capital cost.^{2, 3}

The older types of beehive ovens were built of firebrick and stone, as illustrated

¹ Bennit, H. L., *Minerals Yearbook 1939*, U. S. Bur. Mines, Washington, D. C., 1939, p. 869.

² Porter, H. C., *Coal Carbonization*, Chemical Catalog Co., New York, 1924, p. 58.

³ Foxwell, G. E., *Gas Eng.*, 48, 695-7, 698 (1931).

in Fig. 2.⁴ Coal is charged at the top through a charging hole, and the charge is leveled off through the side door. Gases are driven off by the sensible heat remaining in the floor, oven walls, and roof from the previous charge. Air is admitted through openings in the side door, and combustion takes place largely above the bed of coal, the combustion gases being vented through the charging hole. The coking action is downward. The control of the amount of air admitted through the side door is most important; otherwise a considerable amount of the coke itself would be consumed. The amount of air must be carefully reduced as the coking proceeds to prevent coke loss. The charge of coal is usually 5 to 6 tons, and the time of coking from charge to charge runs from .8 to 72 hours.

The beehive oven loses all the gaseous and liquid byproducts. There is also lost the heat in the unburned portions of these liquid and gaseous products as well as the sensible heat of these gases. Porter⁵ has given the following table:

	Btu
Original heating value, 1 pound coal	13,500
Remaining in 0.63 pound coke	8,060
Burned in oven to effect coking:	
0.07 pound coke	900
0.06 pound tars and oils	1,000
5.5 cubic feet gas	3,200
Total used for coking (of which 1,800 is recovered)	5,100
Miscellaneous losses	340
Total	13,500

The magnitude of this loss led to the development and application of the waste-heat-recovery oven. There are various

forms of this type of oven, many having a duct leading from the charging hole to a master waste-heat flue located above the ovens. The waste-heat flue carries the hot gases to a waste-heat boiler.

Figure 3 illustrates a rectangular waste-heat oven operated by mechanical pushing and leveling machines. Following are data for such an illustration:

Average coal charge, per oven (2 percent water), tons	11.33
Average furnace coke per push, tons	6.95
Average coking time, gross	72 hr. 25 min.
Blast-furnace coke recovery, percent	61.33
Breeze, percent	7.81
	69.14
Pounds of water evaporated per ton coal charged	3,198
Steam pressure, pounds per square inch	190
Superheat of steam, °F	146.1
Feed-water temperature, °F	207

On this basis there is recovered 10.6 boiler horsepower per ton of coal, or 1,760 Btu per pound of coal. This figure compares favorably with Porter's 1,800 Btu per pound of coal recovered.^{2, 6}

The old beehive oven with its loss of by-products and heat and its smoke nuisance led to the development of the waste-heat beehive oven. In order to improve the mechanical handling of the coal and coke, as well as reduce the cost of labor, the rectangular waste-heat oven was developed. However, in spite of these improvements this type of coking required the use of extremely high-grade coking coals, leaving behind coals of inferior coking power.

⁴ U. S. Census Bur., 10th Rept., Coke Section, 1880.

⁵ See p. 109 of ref. 2.

⁶ Belden, A. W., U. S. Bur. Mines, Tech. Paper 50 (1913), p. 20. Pratt, A. D., Met. & Chem. Eng., 16, 27-31 (1917). Harris, G. W., Coal Age, 15, 44-8 (1919). Weihe, C. R., ibid., 18, 479-81 (1920).

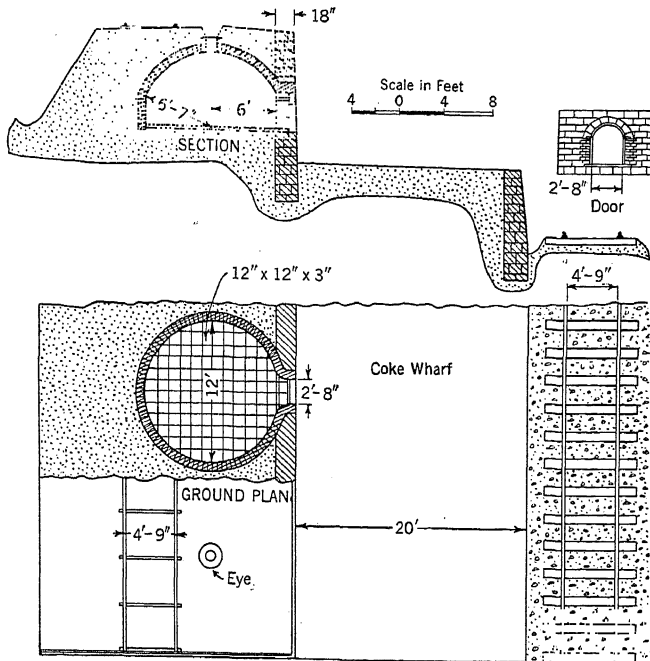


FIG. 2. Diagram of beehive oven.*

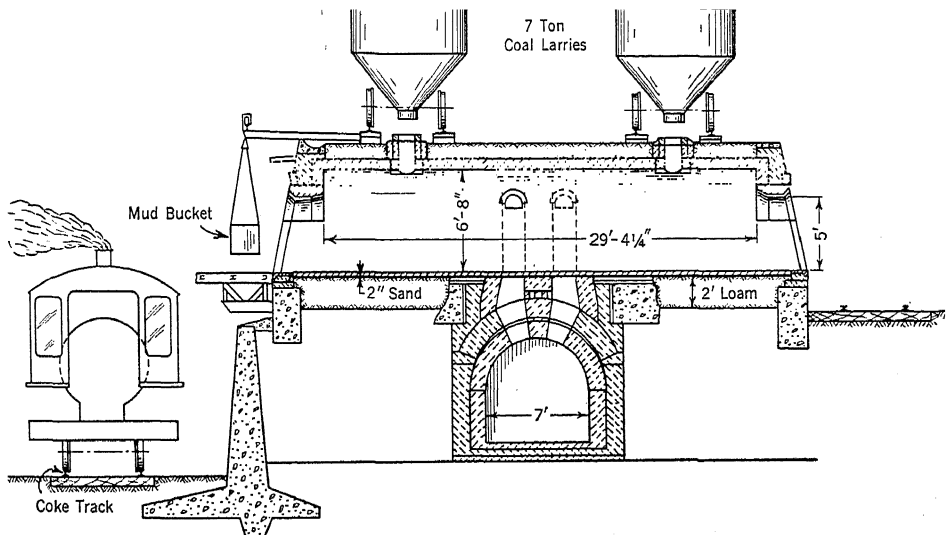


FIG. 3. Horizontal-type waste-heat oven.

Inventors, following the trend, added vertical flues to the waste-heat ovens and pulled the gases driven off the ovens down through these flues located adjacent to the coking chamber. Air was also pulled in, and combustion took place in the flues instead of within the oven. Thus the heat was conducted through a diaphragm or a wall into the coking mass instead of being radiated directly by means of a burning flame.

THE BYPRODUCT OVEN

The byproduct oven as it stands today involves a large number of operations that must be satisfactorily tied together to have a smoothly operating unit. The first consideration is the coal or coal mix to be charged to the oven. The types of coals to be used in each plant must be determined by the individual management. In general the following considerations must be weighed: (a) availability of desired coal; (b) quality of various coals offered (including moisture and ash content and composition, ash-fusion temperature, volatile content of coal, gas and byproduct yield of the coals, expansion forces set up by coal when heated); (c) cost of coal at mine; (d) freight of coal from mine to plant; (e) blending of coals, if desired or necessary; (f) physical and chemical properties of final coke; and (g) storage characteristics of coal.

After all the above factors have been considered and the desired coals selected, the coal is brought into the plant by train, barge, or ship, unloaded, and sent either to storage or to the preparation plant. Coal should first pass under a powerful magnet to remove any tramp iron that might be present. The coal then commonly passes through a breaker, which is usually a rotating cylindrical screen, where it is tumbled about and the larger pieces broken

down until they pass through the screen opening (about 2 inches in diameter), and large pieces of slate, rock, tramp iron, and lumber are cast out at one end. The coal then flows into a pulverizing mill, usually of the hammermill type, where it is pulverized to pass 80 to 90 percent through a $\frac{1}{8}$ -inch opening. Some plants pulverize more finely in order to secure better quality of coke, better mixing, and better control of weight of coal per cubic foot. There are certain practical limits to the degree of pulverization, one of the chief limits being the amount of coal dust carried out of the oven and settling in the coal tar. However, the degree of pulverization must finally be settled at each plant to meet its own conditions.

At some plants where only a single type of coal is carbonized and where an intimate mixture is not absolutely essential, the coal is crushed only to a point where maximum bulk density is obtained. This results in a coal whose overall size distribution consists of particles 2 inches by zero and which gives a bulk density often 15 to 20 percent greater than similar coals crushed to $\frac{1}{8}$ inch or under. Carbonizing this so-called run-of-mine coal is conducive to greater oven and plant capacity.

The coal passes from the pulverizers into bins, each bin containing a certain coal. The coal is fed from the bins by gravity onto moving belts, the width and depth of the coal stream being definitely regulated so that a given weight is discharged per unit of time. When mixing coals, the various regulated streams are fed onto a master belt that conveys the mixed coal to the storage bins located above the ovens. The coal is mixed as it falls at several belt conveyor junctions. Some few plants are equipped with mechanical mixers, but, on the whole, dropping and change of direction of flow are relied upon for mixing.

Occasionally mixing paddles are added to stir up the coal on falling, to aggravate change of direction, etc.

The storage bins for the coal are always located at the end of a battery of ovens and are sufficiently high to permit coal larry cars to run under the bins and clear all steelwork. The bins are supported by heavy steel columns. The bins carry at least 24 hours' supply for the ovens they are arranged to serve. Usually one bin is located between two batteries. Below the bin, level with the top of the coke oven, is located a large platform scale. The larry car that carries the coal from the bin to the ovens is weighed before and after filling; thus a record is kept of the exact weight of coal charged, and where desirable the exact weight of coal sent to each oven can be controlled.

In plants employing volumetric charging methods the larry car is not weighed at each charge but rather filled to a predetermined level corresponding roughly to the capacity of the oven.

The larry car has gone through many modifications since the turn of the century. The oven is equipped with one to five charging holes, and the larry has sufficient hoppers to match the number of charging holes in the oven. Formerly each hopper had its own carriage. For many years, however, all the hoppers have been mounted in a row on one carriage. The carriage is propelled by an electric motor through a gear reduction device. The car travels on standard railway rails fastened to the top of the oven. Modern construction carries the hoppers suspended from an overhead steel structure forming a part of the carriage. The hoppers are conical in shape, and the overhead suspension of the hoppers permits clear space between them and enables workmen to walk around each hopper.

When the loaded larry is in position over the charging holes of the empty oven that is ready to receive the coal charge, the hopper gates are dropped according to a procedure set up in each plant. The coal falls into the oven from the hoppers in stepwise fashion so as to assist in leveling the top of the coal, speed up charging, and prevent to some degree localized packing. When the charging is about complete, the pusher machine is set in front of the oven and a long specially shaped steel structure known as a leveler-bar is inserted at the upper part of the oven through a small leveler-door. The bar is pushed back and forth horizontally through the coal mass by means of cables operated from a motor. The leveler-bar pushes and pulls the coal over the top of the oven, evens the charge, and leaves a clear passage through which the gases resulting from the action of heat on the coal can pass.

When all the coal has left the larry hoppers, the larry is sent back for a load of coal for the next oven and the leveler-bar is removed from the oven just charged, the leveler-door is closed, the charging-hole lids are placed on the holes, and the oven is connected to the hot gas-collecting main by means of a vertical standpipe. This pipe is made of cast iron and in modern practice is lined with a refractory material. There may be two standpipes on an oven, one at each end. If so, two gas-collecting mains are provided, one on each side of the oven battery. These two mains then connect into a common crossover main. This main derives its name from the fact that it carries the gas from the collecting main or mains across and over the pushing machine (which travels on a track in front of the battery) to the byproduct house.

The standpipe is equipped with a simple hydraulically sealed valve located next to the standpipe. This valve is simply a mov-

cup that can be swung by an arm under a gooseneck that fastens the standpipe to the collecting main. Weak ammonia liquor is continuously sprayed into the gooseneck (collecting-main side), and when the cup is out of the way and the opening clear and free the liquor cools the gas to about 180° F, causes some condensation of tar, and saturates the gas with water vapor at this temperature. When the cup is swung into position it almost touches the gooseneck pipe, the cup fills with liquor and shuts off the flow of gas from oven to collecting main, or, should the standpipe lid be open to the air, prevents gas from escaping from collecting main to the air or into the oven.

When the coal falls into the hot oven, gasification begins immediately and continues until most of the volatile matter is expelled. The practices at various coke plants are such that from 1 to 3 percent volatile matter remains in the coke as pushed to yield a product of maximum metallurgical value. The gas pressure at the bottom of the oven may be as high as 1 to 2 pounds per square inch. However, within an hour or two this subsides, largely because the gas finds passage through the coal mass and along the walls. Later the pressure drops to a few millimeters of water pressure, and, often during the coking and always at the end of the coking period, the gage pressure (differential from atmospheric at the same level) is less at the bottom than at the top of the ovens, and at the top less than at the collecting main. This is due to the natural buoyancy of the gas (pressure of hydrogen, methane, etc.) and the buoyancy caused by the high temperature of the gas. The gas pressure is carefully controlled in the collecting main by means of a mechanical regulator located at the junction of the collecting mains and crossover main. For optimum effi-

ciency and plant maintenance, pressure conditions in the collector main should be such that a slight positive pressure be maintained at the bottom of the oven, thereby preventing the infiltration of air and consequent local heating resulting from combustion in the oven chamber. The exhausters in the byproduct house pull the gas through the collecting main to the house, and a slight vacuum with respect to the atmosphere is carried on the crossover side of the regulating valve, enabling an exact pressure, usually amounting to 3 to 20 millimeters of water, to be carried in the collecting main.

By operating a steam jet in the standpipe, thus pulling a suction on the top of the coal, the standpipes can be so operated as to prevent smoke from coming out of the charging holes during charging. This practice is partially successful in eliminating smoke if there is one standpipe and completely so with two (one at each end of the oven). For complete smokeless charging a single- or three-hopper larry should be used. In practice the sequence of operation with a three-hopper larry is as follows: First, the loaded larry car is placed in charging position, the center charging lid is put in place, and the two outside lids are opened. Then the operator cuts the standpipe into the collecting mains, closes the standpipe lid that was open to air, and turns on a steam jet to pull suction on the oven and to prevent the collecting-main gas from backing into the oven. Finally, the larry operator drops the coal from the two end hoppers, and when they are empty he puts on the two outside charging lids, removes the center lid, and drops the center hopper load into the oven. When the coal flow stops, the leveler operation begins and continues until all the coal is leveled in the oven; the leveler is then withdrawn, the leveler door is closed, the top lid is pushed

in place, and the steam jets are shut off. Some successful applications of smokeless charging are accomplished on ovens fitted with a single collector main by means of a duct on the larry car through which trapped gas is conducted to a free charging hole on an adjacent oven that has been temporarily placed under suction.

Ovens are charged and pushed in series. If adjacent coke ovens were pushed and charged in succession, the temperature drop in the heating wall between any two ovens would be very serious. In order to prevent such drops and to even out heats throughout the battery, pushing schedules of various types are employed. One of the most familiar is that developed by Dr. H. Koppers, which operates as follows: assuming a battery of, say, 50 ovens numbered from 1 to 50, the ovens numbered with 1's—1, 11, 21, 31, and 41—are pushed one after the other; when this series is complete, 3 is added and the 4 series is pushed: 4, 14, 24, 34, 44; when this series is complete 3 is added and the 7 series is pushed, which is followed in turn by the 10's, 3's, 6's, 9's, 2's, 5's, 8's, and finally the cycle returns to the 1 series. Marquard has developed a unique mathematical method of a different series.⁷ Many other operators have developed their own schemes of systematic pushing schedules involving dividing the battery or batteries in blocks, etc. All have the same idea in common: (1) to have ovens of approximately the same age on each side of the oven to be pushed; (2) to have the age of the ovens such as to restrain any wall movement should mildly expanding coals be charged; (3) to maintain uniform heats.

The modern oven is about 40 feet long, 18 inches wide, with a taper from one end to the other of about 1.5 to 4 inches. The

height will run from 12 to 14 feet. Such an oven (12 feet high) will contain 720 cubic feet and with coal weighing 50 pounds per cubic foot will hold 18 tons.

The coking speed for ordinary metallurgical coke in such an oven will run from 1.0 to 1.1 inch per hour. Thus, the coking time will be from 18 to 16.4 hours. When the coking is complete and at a fixed time on the schedule, the oven is "pushed" after removing the doors at both ends of the oven. On the pusher side is located the pusher machine that rides on a track the full length of the battery. The machine is large, cumbersome, and heavy, but the equipment is so ingeniously designed that one man can manipulate it. The machine has a motor drive to move it on the track, and it can be set at any point within $\frac{1}{2}$ inch. It is equipped with door removal and handling mechanism since the doors weigh more than a ton. The pusher is also equipped with a coal leveling bar and its driving mechanism. The machine derives its name from the enormous ram that it carries for the purpose of pushing the coke horizontally out of the oven. The ram head has almost the same cross-sectional area as that of the oven, there being a clearance of about 1 inch around the periphery of the head at the pusher or narrow side of the oven. The head is followed by a steel beam over 50 feet long resting on rollers. The bottom of the ram beam is furnished with a rack of teeth that mesh with a spur gear or "bull pinion" driven by motor through a reduction gear. The operator guides the pusher so that the center line of the ram head is approximately in line with the center line of the oven, brings the ram head gently against the vertical coke face, and then allows full power to drive the ram forward, and the coke is pushed ahead out of the oven on the opposite or coke side.

⁷ Marquard, W. B., U. S. Pat. 1,323,711 (1919).

On the coke side a separate machine has removed the door, and a "coke guide" is set in place in front of the oven. The function of this guide is to prevent coke from falling and scattering as it leaves the oven. The guide is built of a steel framework lined with strips of steel 3 to 4 inches wide and spaced 3 to 4 inches apart to prevent warping, is set on wheels, and is manipulated from the coke side door machine. The coke falls from the guide into a "hot car," usually of steel and cast-iron construction, which rests on standard railroad wheel trucks. The car is pushed along by an electric locomotive, equipped with air compressors that furnish air for the car wheel brakes and also operate gates on the hot car. The bottom of the hot car is inclined at an angle of more than 23° to the horizontal, and the bottom inclines away and downward from the coke bench. The coke ram follows the coke to the end of the coke guide. All coke falls into the car, which is slowly moved during the pusher operation so as to spread the coke uniformly throughout the length of the car. When the ram is withdrawn and the doors are replaced, the oven is ready for another charge. The coke car, often called a "quencher car," is run into a tower equipped with sprays, and about 10,000 gallons of water is sprayed onto the coke resting in the car in the space of one to two minutes. The water is hot, and this assists in securing low-moisture coke after draining takes place. The hot car is then run in front of a coke wharf, which is also inclined, the gates of the car are opened, and the coke is allowed to slide out onto the wharf. The coke is removed, screened, and sized and then is ready for use or shipment.

The older coke-oven doors were made of cast iron lined with brick and set against a brick or cast-iron frame. The joint re-

maining between frame and door edge was filled with mud made from clay. The placing of this mud, known as luting, was a long, arduous job. These doors have now been replaced by "self-sealing" ones, which are equipped with a relatively sharp steel angle that fits against the machined face of the door frame. The fitting edge or "knife edge" is somewhat flexible, and if both the knife edge and the flat door-frame surface are kept clean the sealing is practically perfect. Such doors eliminate much of the hard labor about a coke oven.

The heating of the coke oven is supervised by experienced men known as heaters. In all modern ovens all the gas is burned in series, that is to say, alternately on walls of a set of two walls. Gas and air valves are reversed at definite time intervals by automatic machines operated by timing devices. Once a battery is set for a given coking speed, little regulation is required. The heater must, however, be eternally vigilant, watching for over- and underheating, mechanical breakdowns, and accidents, and seeing that maintenance is kept up to prevent upsets in the heating.

The details of oven heating will be developed in detail later in this chapter, since heating has been the controlling element in coke-oven design. For practical purposes ovens are designed to be heated with either coke-oven gas that has been treated in the byproduct house for removal of tar, ammonia, benzene, toluene, xylenes, naphthalene, sulfur, cyanogen, etc., or with "lean" gases such as producer gas (125 to 135 Btu per cubic foot heating value) or blast-furnace gas having a heat content of 90 to 95 Btu per cubic foot. Oven gas may be diluted with water or blue gas, producer gas, air, inert gas, or other gases. The usual heating value of coke-oven gas used for heating ovens ranges from 525 to 550 Btu per cubic foot. It is sometimes diluted to

as low as 400 Btu. The oven gas is introduced at atmospheric temperature in the standard ovens into a refractory channel about 5 inches in diameter lying horizontally about 2 feet below the bottoms of the flues. Gas flows from this "gas gun" into separate vertical holes that terminate in refractory nozzles, which regulate the volume to each flue. Preheated air enters the flue from ports connected to the underlying regenerators, and combustion takes place. The gas gun runs the full length of the oven and is fed from the master gas main from either side or both sides simultaneously. In the underjet oven, the gas to each wall is fed into a pipe in the cellar below the regenerators. One master pipe is supplied to each wall; from this master pipe, individual feeder pipes run to vertical refractory ducts leading to the individual flues. The ducts are located in the regenerator walls that support the flues. The mixing of air and gas in the flues is similar to that in the design using the gas gun.

When lean gas is burned it must be preheated in the regenerators before being mixed with the preheated air. The regenerative system is divided up so that certain up-flow regenerators preheat incoming air and certain other regenerators preheat the lean gas. The gas port arrangement is such as to mix the lean gas and air properly and, in some designs, as in the modern Becker oven, to regulate gas volume. Lean gas and air are fed into the bottoms of the regenerators by means of suitable valving arrangements; the same thing is true of the waste gases leaving the regenerators and the coke-oven gas when it is used for heating. All these valves are connected to rods or cables that operate from a reversing machine, which in turn is actuated by a motor drive operated by a time clock. Reversals are usually 20 to 30 minutes apart, allowing gas to burn in alternate

flues for this period of time. The amount of the various gases burned, etc., is controlled from centrally located valves under the supervision of the heaters. In almost all ovens waste gas (i.e., products of combustion) is removed by natural draft created by a high chimney.

DEVELOPMENT OF THE BYPRODUCT OVEN

The use of the waste-heat oven improved the coke yield from any given coal, but operators began to appreciate that valuable byproducts were being lost when the products of distillation were burned. About the middle of the nineteenth century vigorous and successful attempts were made to recover tar and ammonia. The first really successful coke oven of the byproduct recovery type was the Simon-Carvés oven.⁸ This oven was a simple recuperative type for preheating the air for combustion and was provided with horizontal heating flues located next to the oven wall. (See Fig. 4.) There was no introduction of air or combustion within the oven. The gases evolved from the coking coal were passed through a standpipe and hydraulic main and then pulled through condensers and scrubbers. Gas, free from ammonia and tar, was returned to the ovens for burning to supply the necessary heat of carbonization.

The Simon-Carvés oven was followed by the Coppee, Hüssener, and Otto-Hoffmann ovens. Many Otto-Hoffmann ovens were built in the United States. The byproduct-recovery equipment developed by Otto contributed materially to the success of the oven, which in itself was a notable improve-

⁸ Fulton, J., *Treatise on Coke*, International Textbook Co., Scranton, Pa., 1905, p. 221. Bone, W. A., *Coal and Its Scientific Uses*, Longmans, Green & Co., London, 1918, 507 pp. The Coke Oven Managers' Assoc., *The History of Coke Making and The Coke Oven Managers' Association*, W. Heffer & Sons, Cambridge, England, 1936, 136 pp. Otto, C., *Blast Furnace Steel Plant*, 28, 53-7, 96-7 (1940).

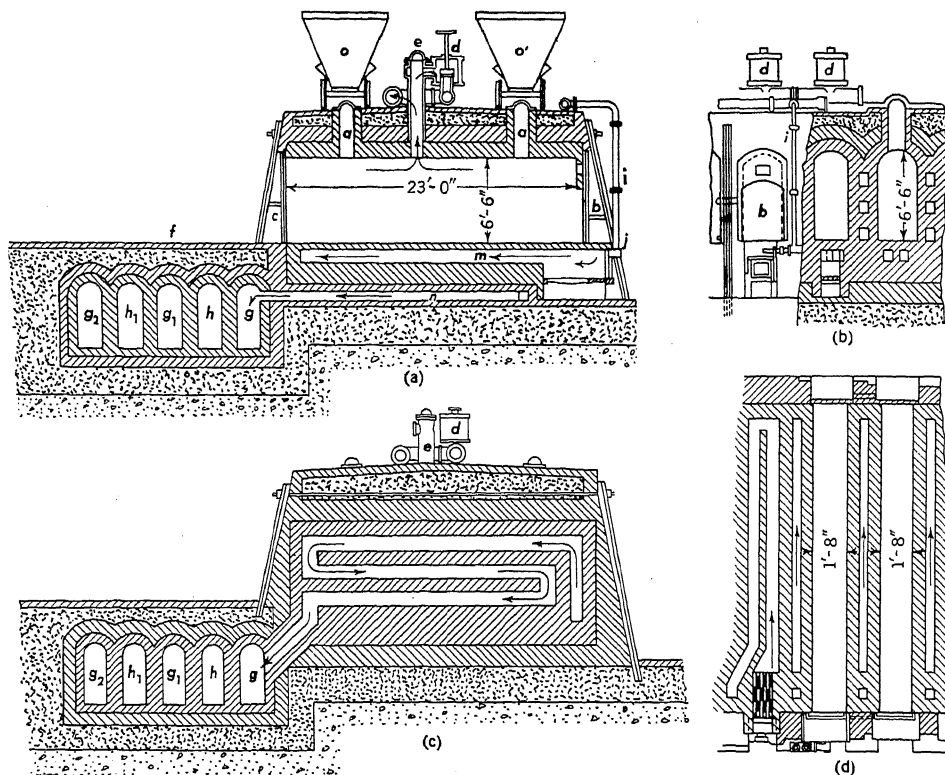


FIG. 4. The Simon-Carvès oven, after Fulton.⁸ *o, o'*, charging laries; *a*, charging ports to oven; *b, c*, doors to each end of ovens; *i*, pipe and tuyères for transmitting gases; *m*, flues under ovens for gases and heated air; *j*, nozzle to mix gases with air in flues *m*; *g, h, g₁, h₁, g₂*, recuperator for smoke and waste heat from flues *n*; *h, h₁*, flues to allow the gaseous products to escape to chimney; *g, g₁, g₂*, flues for passage of air, which is heated on its way by contact with the hot walls of the flues *h, h₁*; *e*, opening on top of oven to collect the gases; *d*, valve to regulate the gases; *f*, coke wharf where the coke is cooled.

ment in the art. This oven (Fig. 5)⁹ had vertical flues and recovered waste heat from the products of combustion by means of regenerators. The two regenerators were long, latticed, brick flues, running transversely of the coking chambers, and at one end each was connected to the chimney by means of a reversing valve. The air was preheated to about 1,000° C. This practice left part of the byproduct gas available for other purposes. The excess gas amounted

to about 40 percent of the total production.

The Otto-Hoffmann oven was modified by Schniewind.¹⁰ It was provided with vertical flues in groups of four, and the fuel gas was fed to the combustion chamber *e* (Fig. 6) below each group of flues.¹¹ This was the first of the "underfeed" type of coke ovens. The fuel gas to each section could be accurately controlled. The regen-

¹⁰ Schniewind, F., U. S. Pats. 627,595 (1899), 644,368-9 (1900), 668,225, 673,928 (1901).

¹¹ See p. 252 of Fulton, J., in ref. 8. Mott, R. A., *Fuel*, 6, 373-80 (1927).

⁹ See p. 236 of Fulton, J., in ref. 8.

erators ran at right angles to the ovens and were independent of the oven brickwork so that the expansion of the oven brickwork would not seriously affect the regenerator brickwork.

The first byproduct ovens to be built in America were Semet-Solvay flue ovens provided with horizontal heating flues in the

not a satisfactory oven for utilizing lean gases such as producer gas or blast-furnace gas, as a heating medium. The velocity of combustion was high in the flues, and this in turn caused a high pressure drop in order to remove the waste gases and necessitated a suction fan to furnish sufficient draft. However, the ovens were easy

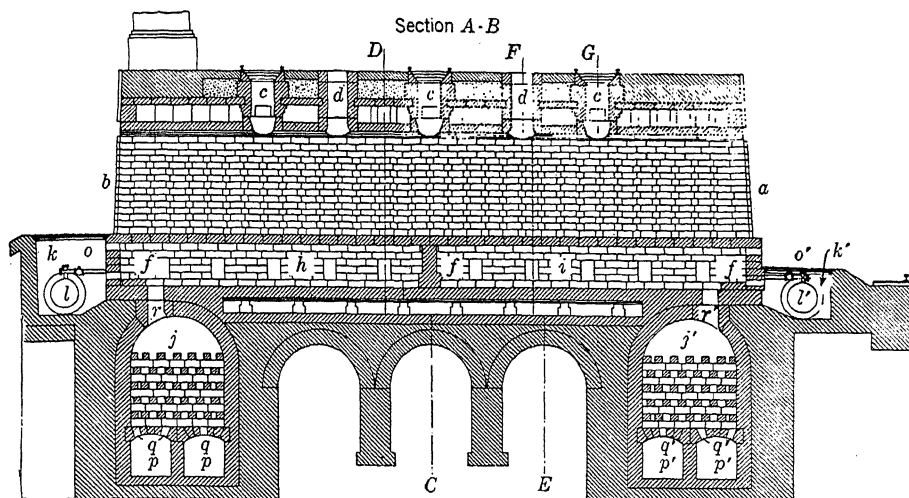


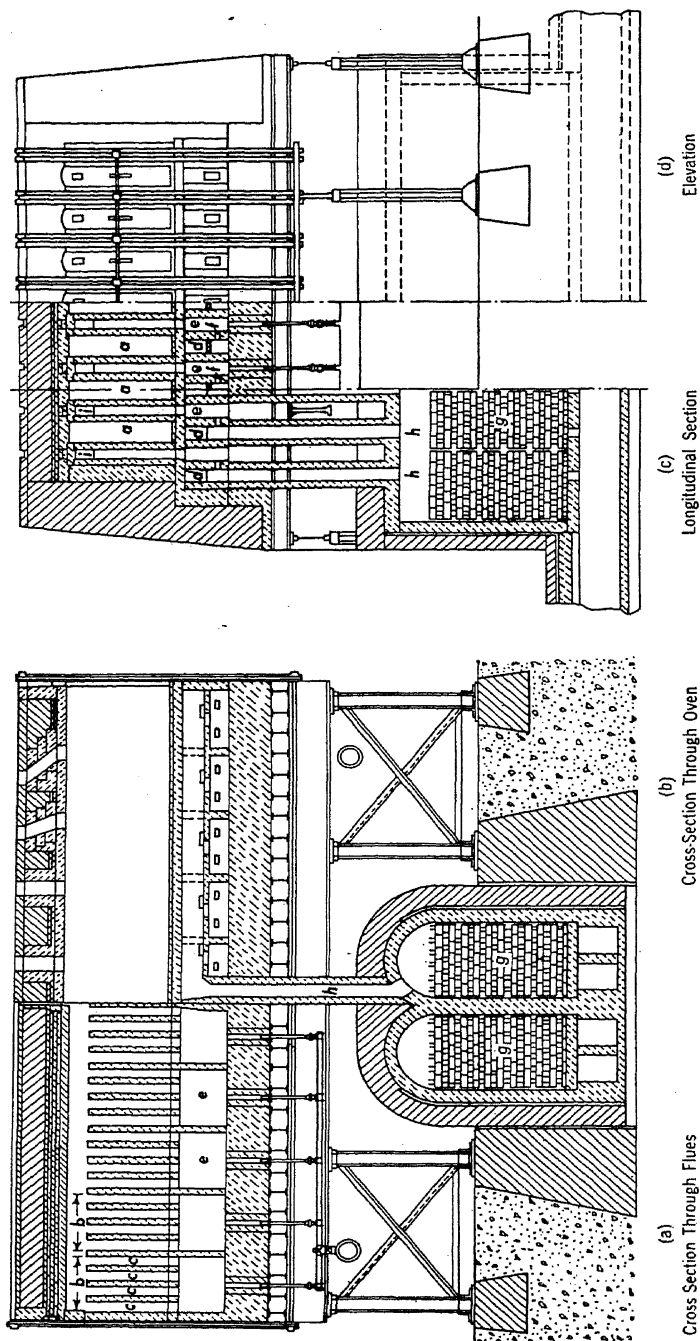
FIG. 5. Longitudinal section of an Otto-Hoffmann oven, after Fulton.⁹

heating walls. The outstanding characteristic of these ovens lay in the fact that each oven was constructed so as to be independent of the ones next adjoining. Each oven had its own individual heating flues, separated from those of the adjoining wall by a solid wall of firebrick, which gave additional strength to the structure and also acted as a heat-storage reservoir. The oven was relatively expensive to build and offered many operating difficulties, owing to the high suction conditions maintained in the horizontal combustion flues. Although each oven of this old Solvay type (Fig. 7)¹² was provided in the course of development with individual regenerators, it was

to repair and in fact could be repaired without affecting the adjoining ovens.

The demand for a cheaper oven that would also burn lean gas such as producer gas and blast-furnace gas was met by the Koppers cross-regenerative coke oven. This oven was first built in America at Joliet, Ill. The Koppers oven was simple and strong. The heating flues were vertical, connecting into a common horizontal flue. The ovens were provided with individual regenerators end to end and parallel with the longitudinal axis of each oven. The reversal of air and waste gas took place at the end of each burning period (usually one-half hour), switching air and gas from one side to the other. Koppers

¹² See also p. 171 of Porter, H. C., in ref. 2.

FIG. 6. Schnievind oven, after Fulton.¹¹

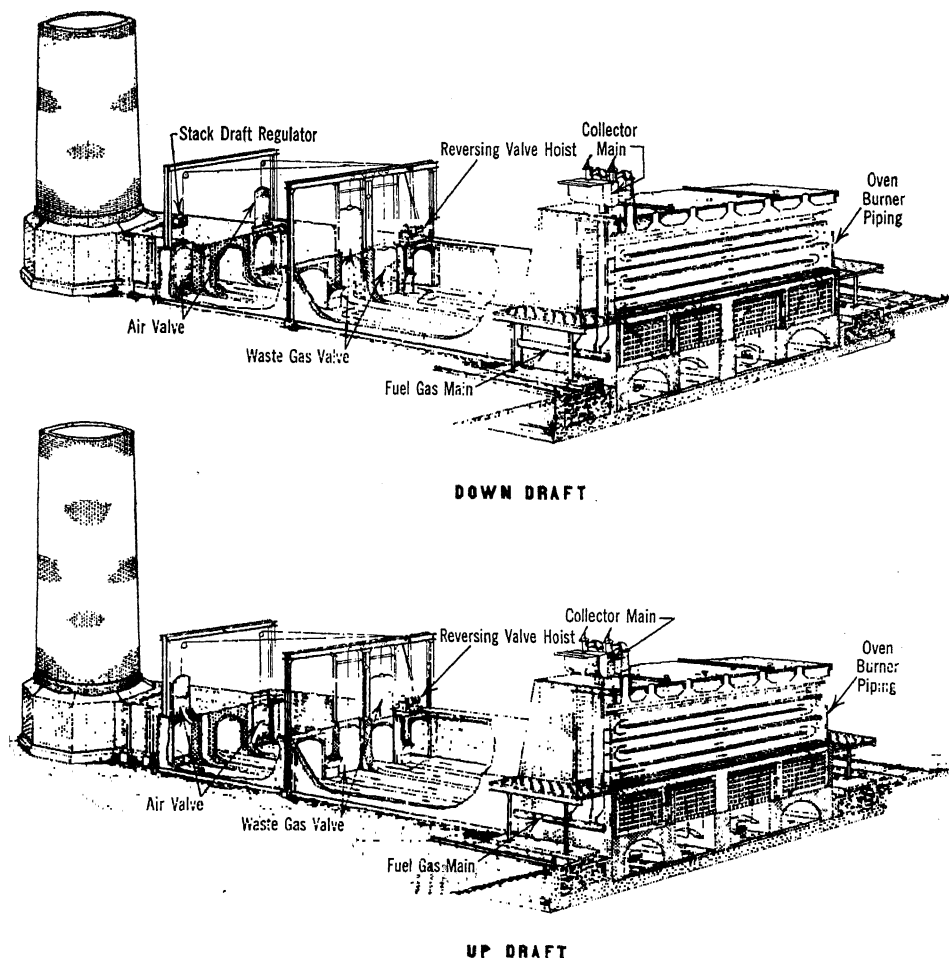


FIG. 7. Semet-Solvay standard double-pass regenerator oven.

added damper bricks to the top of each flue so that the amount of air admitted to each flue could be regulated. Gas was supplied from the side of the battery, through a channel ("gas gun") which extended below the vertical flues, a removable gas nozzle being fitted to each vertical flue (Figs. 8 and 9).

This oven was very successful. Its ruggedness and simplicity of construction insured a long operative life. Owing to the

large size of the horizontal flue required when heating with blast-furnace gas, the oven structure was definitely weakened at the horizontal flue.

Denig¹³ analyzed the difficulties of the old form of the Koppers oven as follows:

Because of the demand for a larger capacity oven and in order to handle lean gas, such as producer gas or blast-furnace gas, it

¹³ Denig, F., *Iron Steel Engr.*, **15**, No. 10, 32-53, 63 (1938). Cf. Wilputte, L., *Blast Furnace Steel Plant*, **27**, 471-86 (1939).

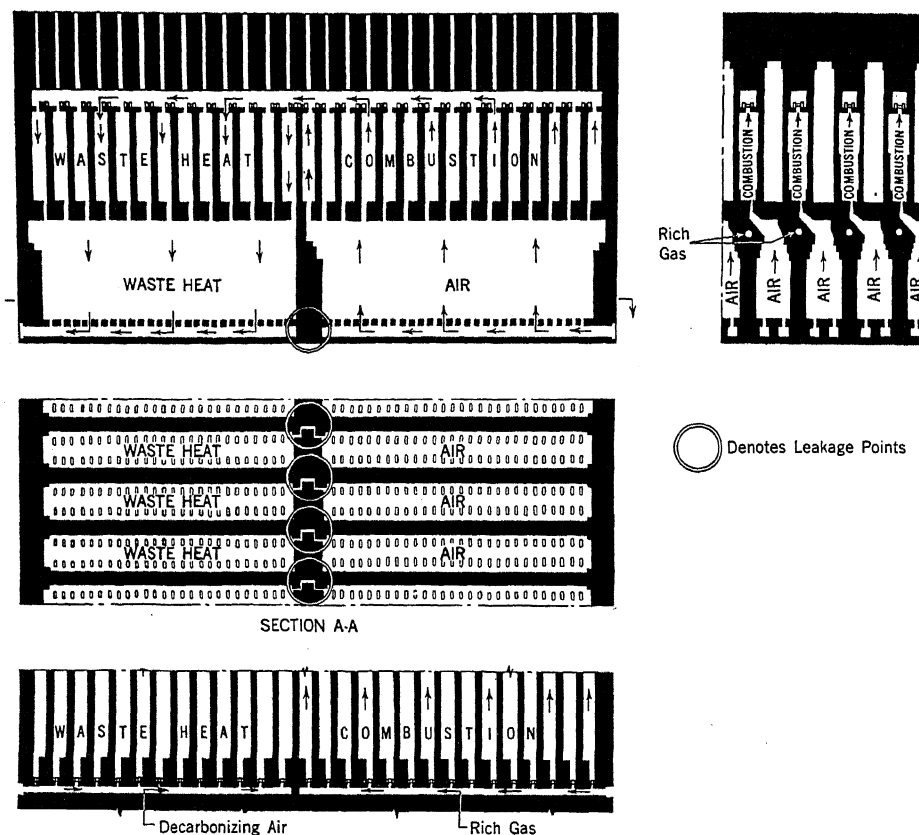


FIG. 8. Old Koppers oven with rich-gas heating.

was necessary to considerably enlarge the conventional horizontal flue located near the coal level in order to prevent excessive flow velocities, and this resulted in a weakening of the upper structure. Also, in order to control the volume of fuel gases entering the individual flues, it was necessary to use sliding bricks where the vertical flues entered the horizontal flue, and this in itself considerably increased the pressure differential between the heating and horizontal flues and consequently the pressure differential throughout the battery. The horizontal flue for blast-furnace-gas practice became so large as to render its use both impractical and dangerous to the life of the oven.

In comparing an old Koppers oven having a capacity of 18 tons of coal per day, when

using coke-oven gas as the underfiring medium, with a modern oven of 28 tons of coal per day throughput while using blast-furnace gas for underfiring, we find that the volume ratio between their waste gases is in the proportion of about 1 to $2\frac{1}{4}$. In order to maintain comparable velocities in the two horizontal flues, the horizontal flue of the larger oven would have to be not less than $2\frac{1}{4}$ times the area of the old Koppers horizontal flue. This entire space would be unsupported and so weaken the horizontal flue that it could be easily pushed in, and such design was therefore out of the question. Experience had already taught that a horizontal flue of say 13-inch height, even in small ovens, was altogether too weak. Experience has also proven that this is even much more

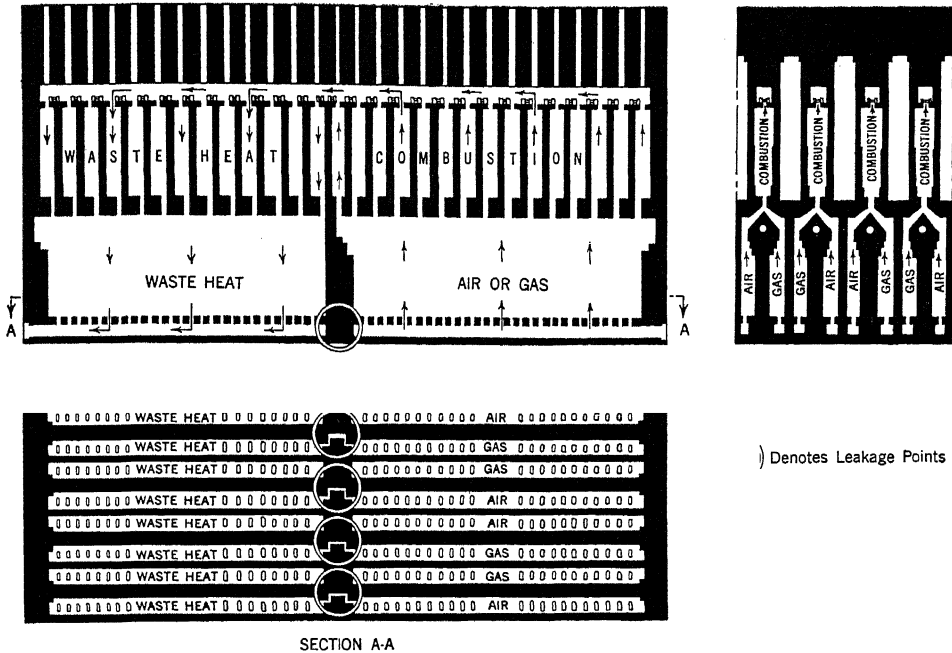


Fig. 9. Old Koppers oven with producer-gas heating

serious for the higher ovens because any given angular distortion is reflected in the horizontal flue in proportion to the oven height.

Another serious defect of such a large horizontal flue is that it materially retards the coking of the coal mass lying adjacent to it (as much as one or two hours in respect of the balance of the coal). This causes high heat consumption for the underfiring and a nonuniformly coked charge and reduction in plant throughput.

One of the early attempts to improve the Koppers oven was made by the Wilputte Coke Oven Corporation.¹⁴ Individual regenerators were furnished to each flue. Air was forced to each regenerator by means of a central blower and piping equipped with suitable orifices. On May 22, 1919, the U. S. Circuit Court of Ap-

peals adjudged this oven to be an infringement of H. Koppers U. S. Patent No. 818,033. This decree limited the number of such ovens that were built under these Wilputte patents.

Since the top horizontal flue was essentially the same as that of Koppers, the Wilputte horizontal flue was no improvement. Designers throughout the world then sought various means of overcoming the horizontal-flue limitations. A number of engineering concerns seized on the idea of placing two short two-divided Koppers ovens end-to-end so as to reduce the cross-sectional area and the length of the horizontal flue. This practice was followed by Wilputte Coke Oven Company, as exemplified by their design at Gary, Ind.; by Semet-Solvay, as exemplified by their design construction of the plant for the Great Lakes Steel Company at Detroit, Mich.;

¹⁴ Wilputte, L., U. S. Pats. 1,212,865, 1,212,866 (1917). See also pp. 205-8 of Porter, H. C., ref. 2.

by Dr. H. Koppers in numerous plants designed and built by him in Germany; and in one American plant built by Koppers Company of Pittsburgh.

In 1921, the Koppers Company in America tried this design in a small plant and H. Koppers in Germany for a time adopted a construction (the double-divided oven, sometimes called the four-divided oven) wherein instead of having only two regen-

erators per oven, that is, a coke-side and pusher-side regenerator, and of burning from the coke side and pusher side, the oven was divided into four heating sections (as shown in Figs. 10 and 11) or actually into what was equivalent to two short Koppers ovens end-to-end. In this design, gas could burn, for example, simultaneously in sections A and D and waste gases flow downwardly into B and C, and thence to

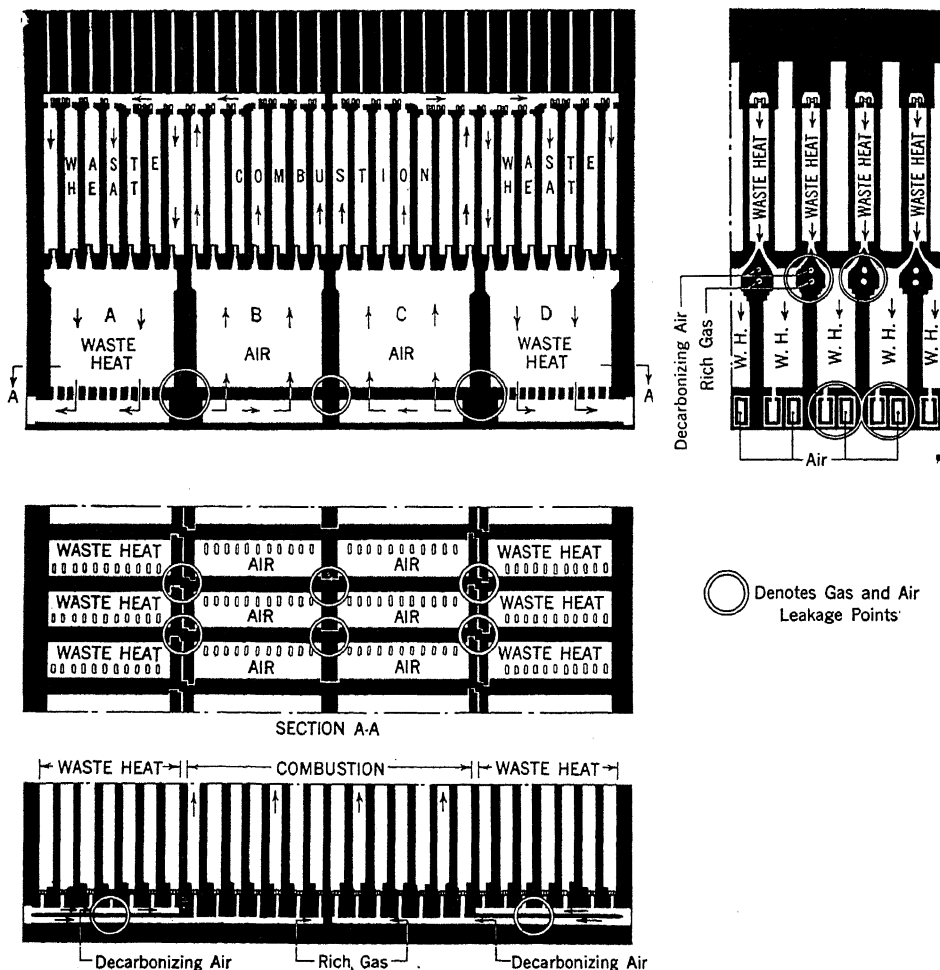


FIG. 10. Koppers double-divided oven with rich-gas heating.

the stack canal. Another combination would be to burn in *A* and *C* simultaneously as the waste gases pass to *B* and *D*. In either system, of course, reversals would take place. This design reduced to some extent the horizontal-flue cross-sectional

flue there are added thereto other volumes of waste gas being discharged into the common horizontal flue from still other heating flues, and in order to maintain the required rate of flow there must be an increasing pressure drop from the far end of the hori-

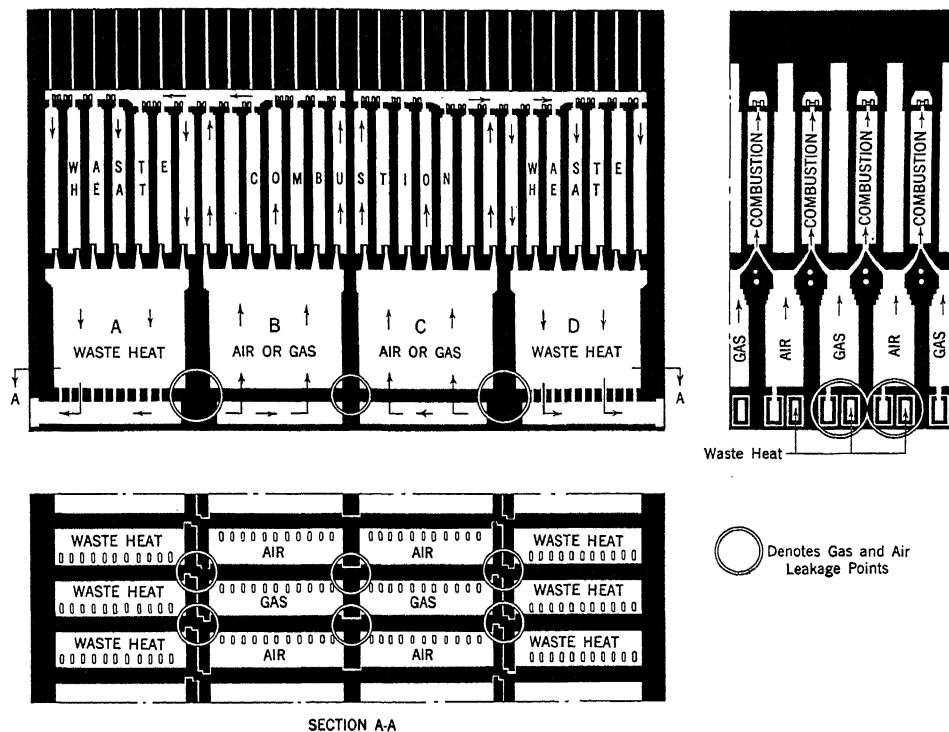


FIG. 11. Koppers double-divided oven with blast-furnace-gas heating.

area for ovens of modern size but it still retained the structural weakness and other drawbacks previously cited.

Figure 12 indicates the area of the horizontal flue for a double-divided oven that is 13 feet high and uses blast-furnace gas as the heating medium. Designers found that further reduction of the horizontal-flue area increased the pressure drop from the vertical flues to and through the horizontal flue for the following reasons:

As waste gas flows along the horizontal

zontal flue, where there is a minimum flow, to its discharging end at which point there is a maximum volume of waste gas. In a Koppers oven this maximum volume would be the total discharged from fourteen flues or, in the double-divided oven, from seven flues. The more heating flues that a horizontal flue serves, for any given size, the greater must be the pressure drop throughout that flue, according to the Bernoulli theory for gas flow.

In order then to control the volume dis-

charged by each vertical flue into the common horizontal flue, it is necessary to cut down, progressively in the direction of flow, the port area of discharge into the horizontal flue. This is done by means of the familiar sliding brick, which are pushed over the openings so as to leave only enough space to discharge the requisite amount of waste gas into the horizontal

with the old Koppers oven (assuming the oven to be of the same size as the old Koppers oven), but when the oven is enlarged to the present-day dimensions, and especially when heating with blast-furnace gas, such differentials become exceedingly high and unsatisfactory for good and safe operation. (See Figs. 13 and 14.) The diagrams represent actual readings of pres-

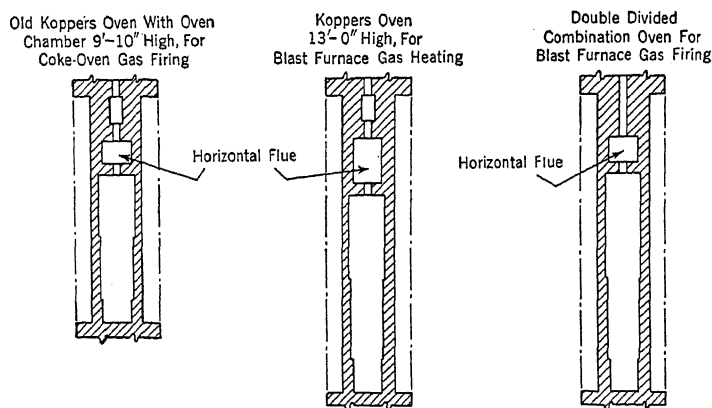


FIG. 12. Areas of horizontal flues for various designs.

flue. A pressure drop in the restricted area, which is set up by the sliding brick, is repeated on the downflow side through the restricted openings there, and the sum of the two drops through the up- and down-flowing vertical flue ports and the horizontal flue represents the largest part of the pressure drop through the combustion system.

In building the double-divided oven, there would be seven flues discharging into a common horizontal flue. Should the horizontal flue remain the same size as the old Koppers horizontal flue, then the differentials would be less but the structural weakness would remain. If the area of the horizontal flue is cut in half there is some improvement in structural strength but the pressure differentials remain the same as

sure conditions within the old Koppers oven using producer gas and within the Koppers double-divided oven using blast-furnace gas for heating the ovens. From these readings the differentials can easily be computed. With coke-oven gas these differentials are, of course, smaller, but it must be remembered that the heating of the ovens with low-Btu fuel gases must be considered, and the diagrams demonstrate the high differentials set up by the two systems of heating mentioned.

The large pressure drop created between the up- and the downflowing flues and the horizontal collecting flue is caused by two factors: first, as already mentioned, by the restricted area by the regulable sliding-brick opening; and second, by the whirling and baffling effect of the hot gases as they

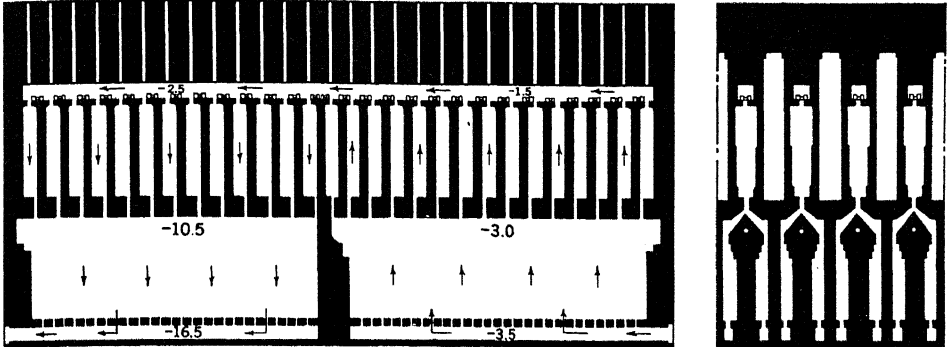


FIG. 13. Pressure survey in a Koppers oven when burning producer gas with 19 tons of coal per day throughput. Pressures in millimeters of water.

strike the sliding brick and the brickwork supporting it as well as the opening it controls. Actual measurements show that a substantial amount of the pressure drop is due to the baffling effect of this brickwork. Therefore, the minimum pressure loss can be secured only by having vertical flues with tops practically entirely open.

In order to eliminate the effect of the restricted area of the sliding-brick openings, the designer might be tempted to eliminate the sliding brick entirely and to open up the ports leading from vertical flues to the

horizontal flue and to provide for all the regulation at the bottom of the flues, i.e., at the air and gas ports. However, this will not give satisfactory regulation. If the flue bottom-port areas are proportioned according to the taper of the oven, then the upflow of air (or gas) or downflow of waste gas will depend on the pressure differential between the top of the regenerator and the horizontal flue. The pressure changes progressively along the horizontal flue, and as a result there will be unequal flows through the different vertical flues. If the

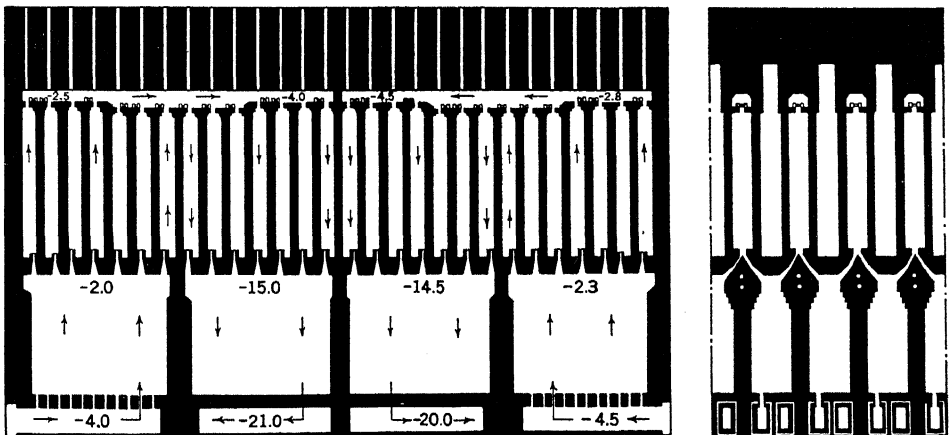


FIG. 14. Pressure survey in a Koppers double-divided oven when burning blast-furnace gas with 21 tons of coal per day throughput. Pressures in millimeters of water.

air-port areas are changed to correct this condition, then this setting will be good for only one fixed coking time and only one kind of fuel gas. If either the coking time or the fuel gas is changed, the setting becomes incorrect. Moreover, the high differentials remain because in order to regulate the various flows restrictions must be made in port areas, and differentials of pressure result. It becomes evident, therefore, that regulation at the heating-flue bottoms with minimum loss of pressure can be successfully achieved only with practically zero pressure drop along the horizontal flue, and this in turn really means elimination of diverse flow velocities at the tops of the flues.

There are now operating in the United States a number of double-divided ovens as exemplified by Fig. 15. In this figure the flow and counterflow are indicated by the shading. This oven has been built in several installations by the Wilputte Coke Oven Corporation, and modifications of this principle have been incorporated by Semet-Solvay Coke Oven Corporation. Since January 1, 1940, these two organizations have combined and are now building the ovens shown in the diagram.

However, in order to improve the design of the coke oven as a whole and to eliminate the various faults cited in the above discussion, designers have turned toward the design of a combustion system having a low differential pressure drop. This type of oven is known in the trade as the "low-differential" oven. There are two outstanding designs of such ovens. The first is the familiar hairpin type, which has been built extensively throughout Europe and Asia; the second, the "Becker" oven, has been built throughout many parts of the world and is, of course, exceedingly well known in America. The number of by-product coke ovens by types in the United

States in 1939 is shown in Table I.¹⁵ The capacities shown were estimated by the writer.

A good example of the hairpin flue type of oven is the Otto oven illustrated by

TABLE I

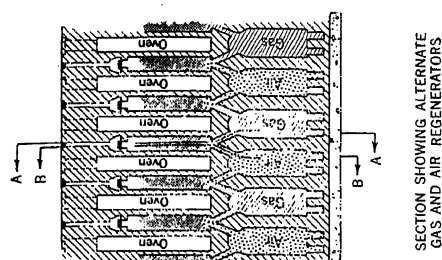
NUMBER OF BYPRODUCT COKE OVENS IN THE UNITED STATES BY TYPES OF OVENS,¹⁵ AS OF JULY 1, 1939

Type of Ovens	Number of Ovens
Koppers (including Becker)	10,061
Semet-Solvay	1,832
Wilputte	771
Cambria	120
Improved Equipment	60
American-Foundation	55
Curran-Knowles	46
Parker-Russell	27
Roberts-Morrissey	25
Piette	8
Total	13,005
Beehive ovens	10,816
Estimated full carbonizing capacity	
	Tons per Day
Byproduct plants	170,000
Beehive plants	27,000

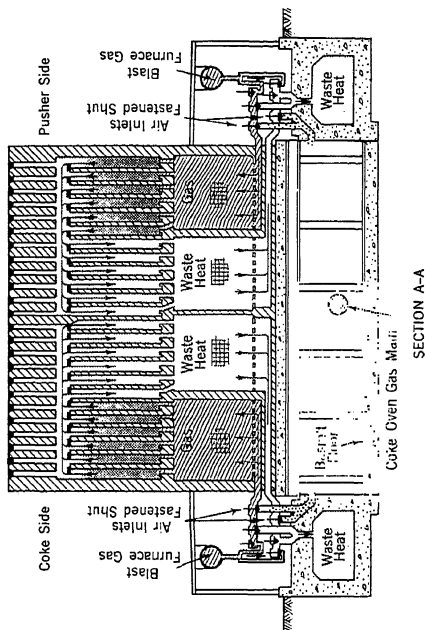
Figs. 16a and 16b, and the flow of the gases is self-evident upon examination of the diagram. The individual hairpin flues in combination with single regenerators for each wall were first invented by Dr. Koppers of Essen, Germany,¹⁶ and were described by Otto⁸ in his paper dealing with the history of coke ovens. It will be noted that the oven uses the high and low burner principle, as is shown in the Wilputte diagram, and the oven also has liners of uniform thickness in contrast to previous

¹⁵ U. S. Bur. Mines, *Directory of Byproduct Coke Plants in the United States, July 1, 1939.*

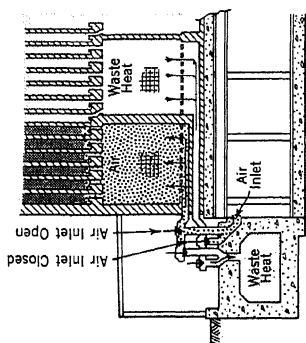
¹⁶ Koppers, H., Ger. Pats. 189,148, 189,325 (1906).



SECTION SHOWING ALTERNATE GAS AND AIR REGENERATORS

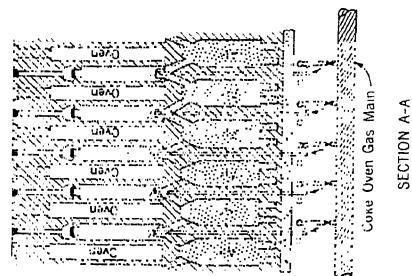


SECTION A-A



AIR AND WASTE HEAT CONNECTIONS TO AIR REGENERATORS

SECTION B-B



SECTION A-A

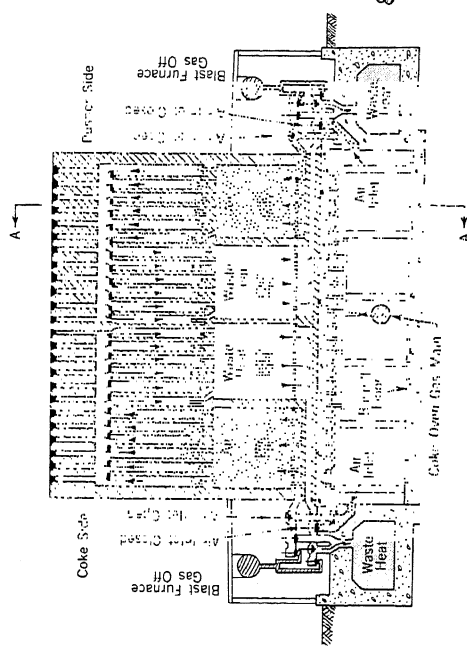


FIG. 15. Willputte oven.
 Above. Lean-gas underfiring.
 At right. Coke-oven-gas heating.

American practice. No Otto ovens have been built in the United States, although many have been built in Europe and Asia. But those built in Europe and Asia differ radically in design from the oven offered to the American trade. For example, the

The construction of this oven is interesting in many respects, inasmuch as it is an ingenious solution of narrow regenerators located side-by-side.¹⁷ The oven indicates some low differentials of pressure, but its designers have not been able to provide

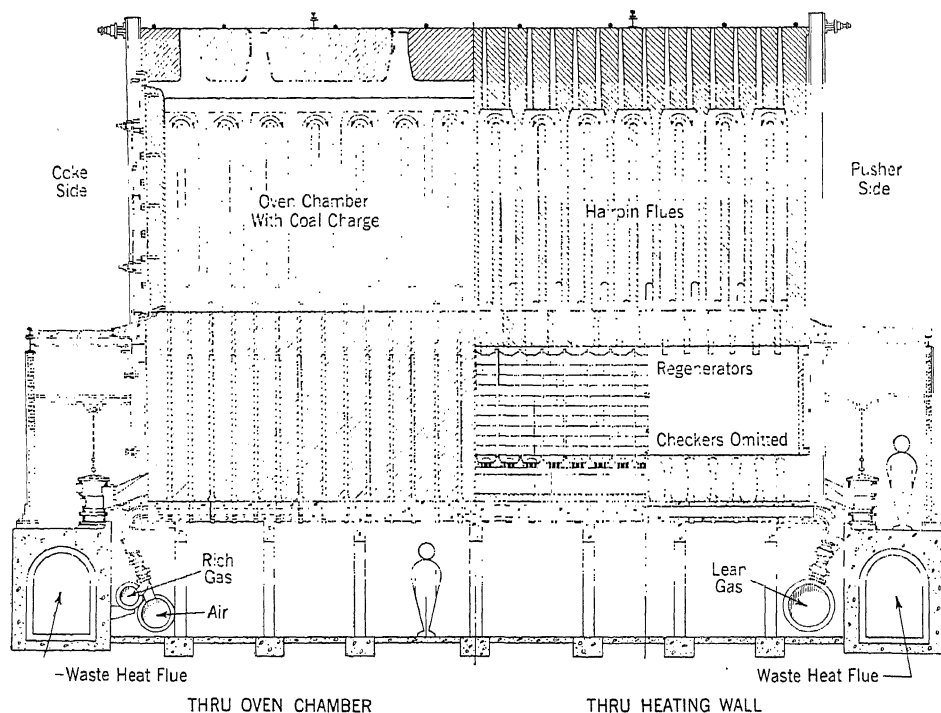


FIG. 16a. Otto oven.

oven is of the underjet principle, i.e., the gas is fed to the oven by means of ducts beginning vertically in the supporting mat; but these ducts are curved in the American design, whereas in European and Asiatic design they rise vertically and enter straight into the coke-oven flue (Fig. 16c).

Figures 16d and 16e show the two reverse conditions of lean- and rich-gas heating. It will be noted that in lean-gas heating the upflow lean-gas regenerator lies next to a downflow waste-gas regenerator.

for the insertion of a blanket of air or an air-filled regenerator between downflow waste gas and upflow lean gas.

The Koppers-Becker oven is a combination oven in which there are incorporated all of these desirable features. A ready inspection of the flow diagram (Figs. 17 and 18) will quickly demonstrate the simplicity of the combustion gas system. All the flues in any burning wall burn si-

¹⁷ See also Rugg, D. M., U. S. Pat. 1,393,455 (1921).

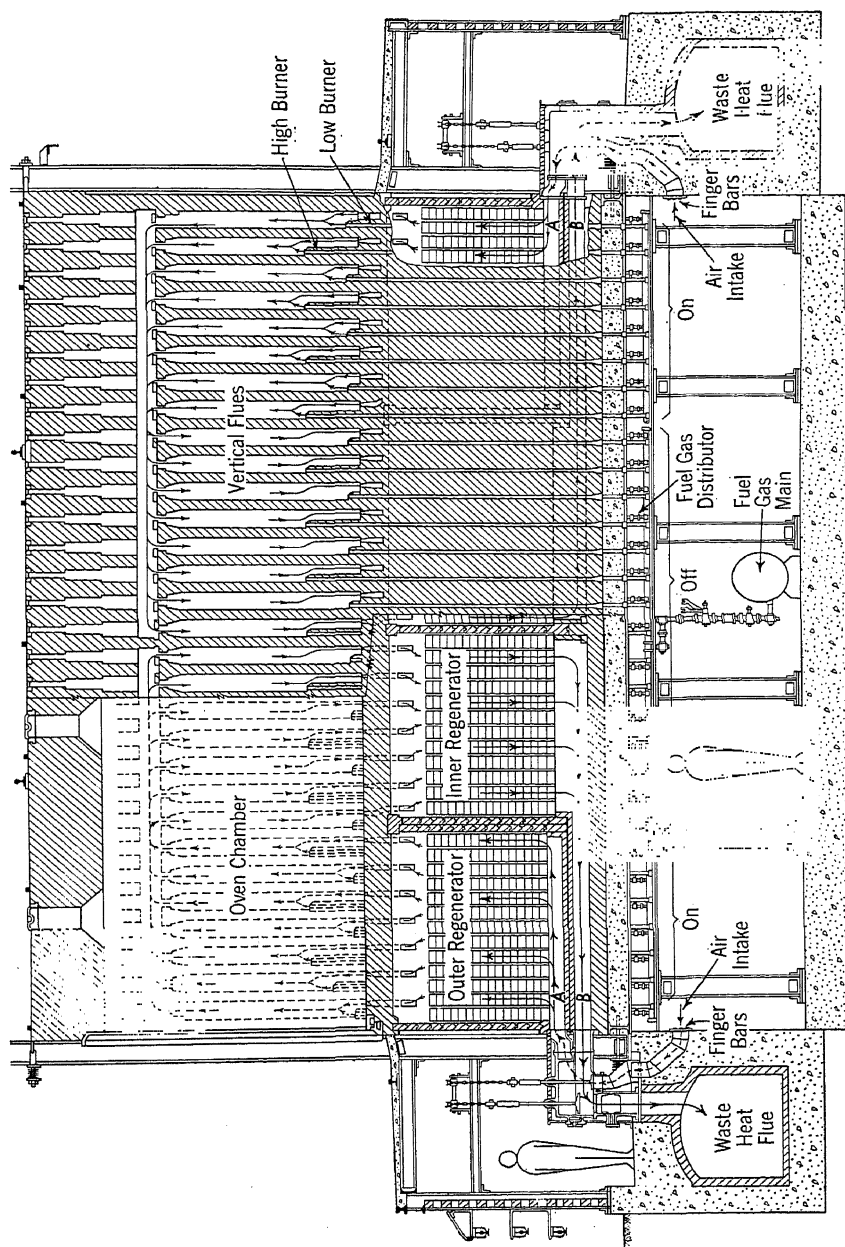


FIG. 16b. Otto-Wilputte oven with high and low burners for burning coke-oven gas.

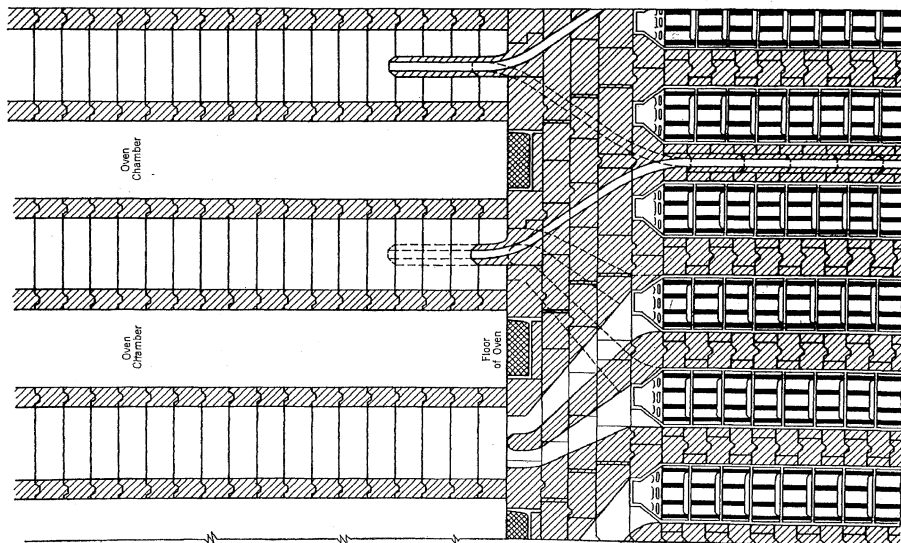


FIG. 15c. Otto oven of American design for feeding rich fuel gas to flues.

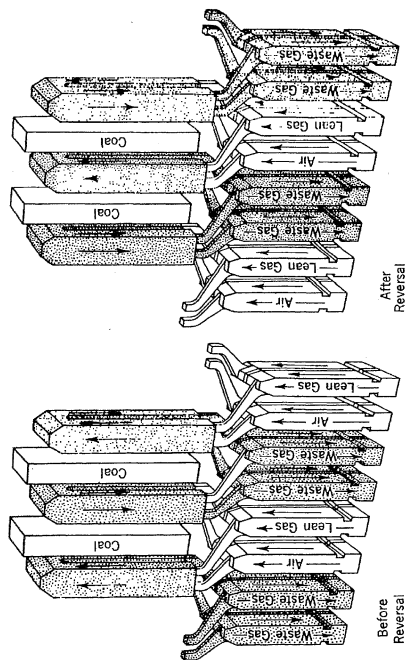


FIG. 16d. Otto oven, showing flow of gas and air in the flues and regenerators in the compound oven when fired by lean gas, before and after reversal.

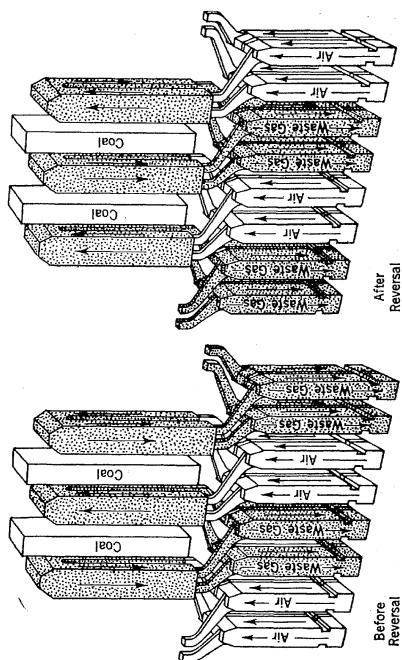


FIG. 16e. Otto oven, showing flow of gas and air in the flues and regenerators in the compound oven when fired by rich gas, before and after reversal.

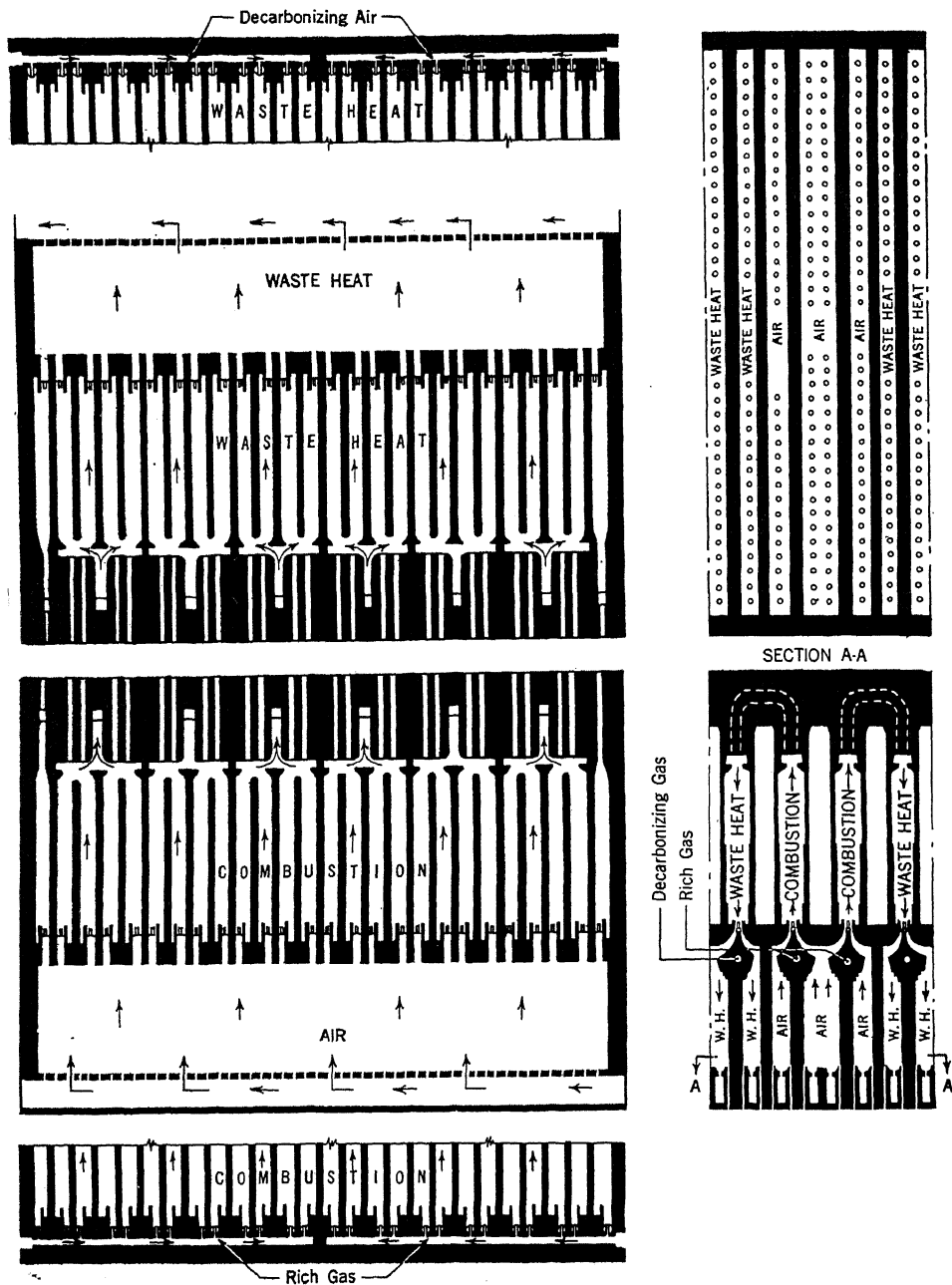
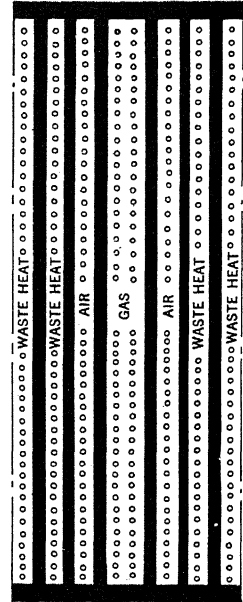
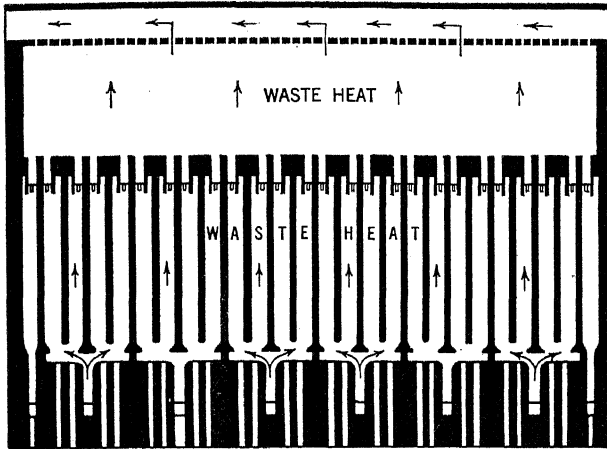


FIG. 17. Flow diagram of Koppers-Becker oven when burning coke-oven gas.



SECTION A-A

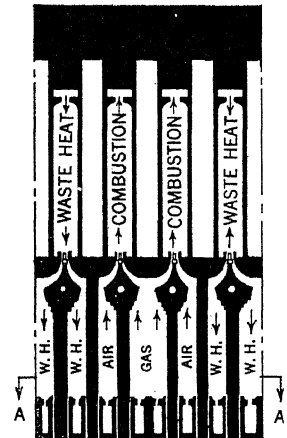
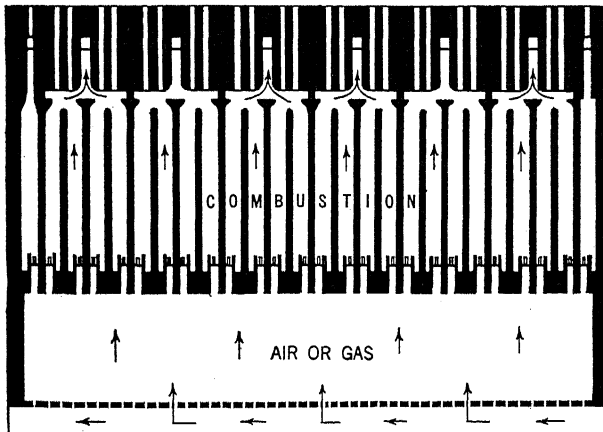


FIG. 18. Flow diagram of Koppers-Becker oven when burning producer or blast-furnace gas.

multaneously upward while all those in the adjoining companion or twin wall are filled with waste gas flowing downward. The upflowing and downflowing flues are separated by an oven full of coal; the fuel gases,

both high and low Btu, are blanketed on each side by air flowing in the same direction as the fuel gas. In the Koppers-Becker oven an upflowing and downflowing wall are connected by crossover flues. The

whole combination of the upflowing and downflowing flues and of the regenerators and crossovers may be easily conceived of as a book, the outside covers representing flues and regenerators, the shelfback representing the crossover sections, and the leaves representing the coal. The whole combination can be laid out flat, as by opening a book, and the flow shown on a

with air and also because both lean gas and air are carried under identical pressure conditions. The method of control of combustion in the flues is simple. The air is regulated by a single port and plug in each flue. When heating with oven gas and the gun-conduit system of feeding fuel gas to the flues, the gas is controlled to each flue individually by means of refractory noz-

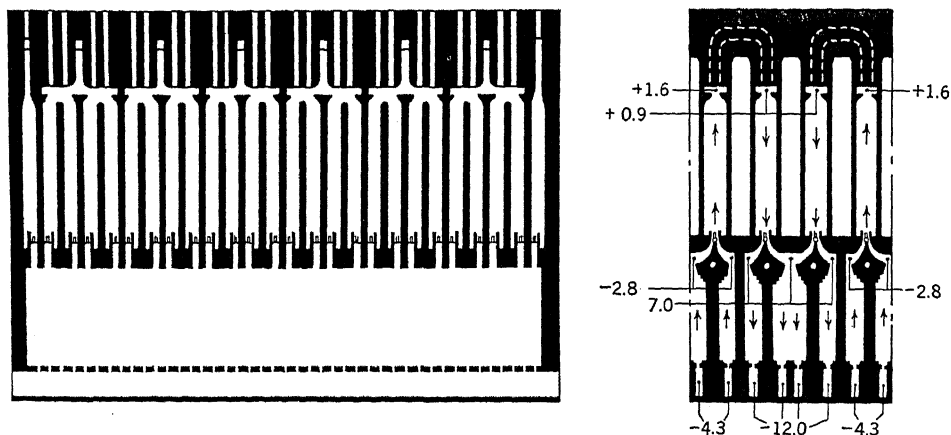


Fig. 19. Pressure survey in a Koppers-Becker oven when burning blast-furnace gas with 24 tons of coal per day throughput. Pressures in millimeters of water.

flat plane. Another interesting viewpoint of the Koppers-Becker oven is that it can be likened to a hairpin oven with the paired flues turned at right angles and having certain of such adjacent flue pairs grouped together with a layer of coal located between the individual flues of the pairs comprising a group. This arrangement of twin walls makes possible the ideal grouping of regenerators beneath them.

The regenerators and sole flues are continuous for uninterrupted inspection from end-to-end and are accessible throughout their entire extent. There can be no cross-leakage of fuel gas into the waste gas or the air in the Koppers-Becker oven because of the simplicity of the flow system and the care taken to blanket the fuel gases

zles. When operating with blast-furnace or producer gas, the simple port and plug arrangement cited above is fully adequate. Hand regulation and guesswork are eliminated. Nothing needs regulating. The various port areas can be easily computed, and, in the event that a change in their cross section is required, it can be quickly accomplished by exchanging plugs. In those instances where the underjet under-firing system is used, the regulation of fuel gas is equally simple.

Figure 19 shows a pressure survey of a Koppers-Becker oven burning blast-furnace gas. Since the flow of gases through this horizontal passage exerts no such influence on the discharge from the vertical flues as does the common horizontal flue in the

other designs, as before explained, this horizontal flue can be of small dimensions. (See Fig. 14 and compare with Fig. 12.) The old function of the horizontal flue to collect waste gases from one group of flues and to convey them horizontally over into therewith-connected vertical flues is eliminated, and the gas flow in the heating system at any coking time or condition or variety of heating gas is not hindered. In the Becker oven this horizontal flue is structurally and functionally absent, the waste gases merely passing more vertically than horizontally through such space, which is no larger than is necessary to equalize pressure over a group of four flues.

THE UNDERJET OVEN

The latest design (1935) of the Becker oven includes the so-called underjet burner. In this design the rich heating gas is fed to each flue by means of a duct passing through the foundation and upward through the regenerator wall to the base of the flue where mixing of air and gas takes place. When lean gas is burned it is introduced through the lean-gas box at the base of the regenerators. Denig¹³ has explained the change to the underjet method of feeding rich gas as follows:

In the gun-flue construction, the old clay nozzles were always a source of trouble largely as a result of their tendency to swelling and deformation under the influence of heat. This condition has been eliminated by the introduction of the silica nozzle but it is true, nevertheless, that if a radical change is made in coking time there should be some change in nozzle settings, and this is always a laborious procedure since such operation must be effected from the top of the battery. Feeding the gas to the flues by means of the underjet ducts eliminates the necessity of patching the gun-bricks, and in the event that a radical change in coking time is demanded, the regulation of the gas can be easily carried out from beneath the oven.

The gas to each flue can be exactly controlled by suitable orifices or other metering devices inserted in the gas line leading to each flue duct. The general design of such an oven is shown in Fig. 20. This drawing shows the underjet features in detail. It also shows a modern type of coal larry car, a gas main with liquid-sealed gas offtake valves for each oven, and a double collecting gas main for smokeless charging.

SMALL-SCALE OPERATIONS

INTERMITTENT RETORTS

The small intermittent retort has almost passed out of American practice. The advent of natural gas and large central coking plants has almost eliminated this type of coking unit. Intermittent retorts were built in four forms: (1) stop end; (2) through; (3) vertical intermittent; and (4) inclined. The first two forms are variations of horizontal retorts. All four types have been well described by Meade.¹⁸

THE U.G.I. INTERMITTENT VERTICAL CHAMBER OVEN

Carbonization of coal in intermittent vertical chamber ovens is a method that has proved well adapted to the requirements of small and medium-sized gas works. In these ovens gravity does the work of charging and discharging, so that special machinery for the purpose is unnecessary. The coal is charged into the ovens from a movable larry running on rails on the top of the battery and is allowed to remain in the oven for the proper carbonizing period, about 12 hours, after which the coke is discharged into a car beneath the ovens and transported hot to the quenching station.

This type of oven has a considerable rec-

¹⁸ Meade, Alwyne, *Modern Gas Works Practice*, Benn, London, 2nd ed., 1921, 815 pp.

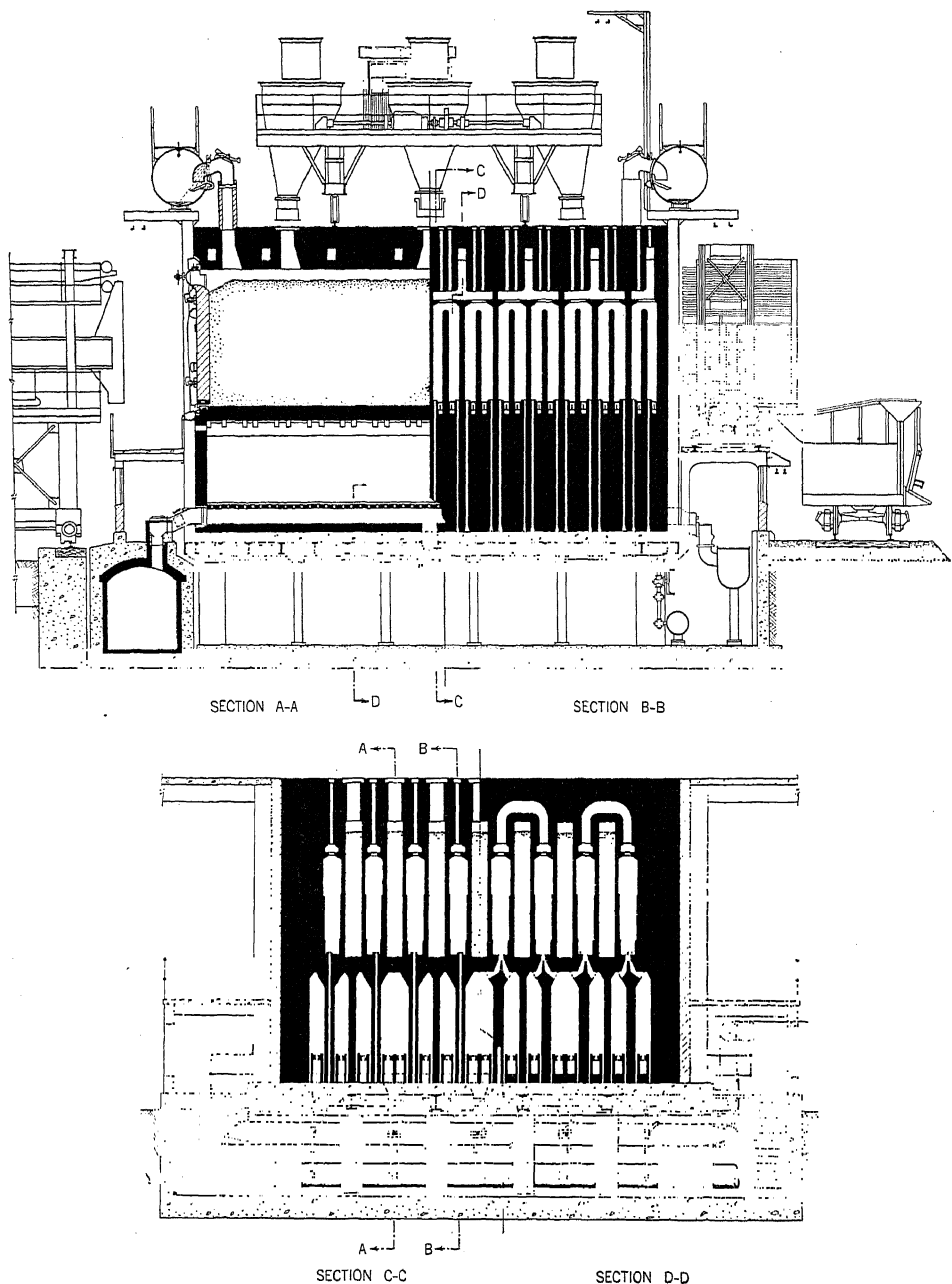


Fig. 20. Koppers-Becker underjet oven.

ord of experience behind it, being a development of the intermittent vertical retort introduced in this country in 1910. It was developed in Germany around 1918 when the first World War had created a shortage of manpower and labor saving was urgently required. Some four hundred or more installations have been made abroad by the Didier Company, and eight installations (three in one plant) have been made in the United States by United Engineers and Constructors, Inc. One of them is illustrated in Fig. 21.

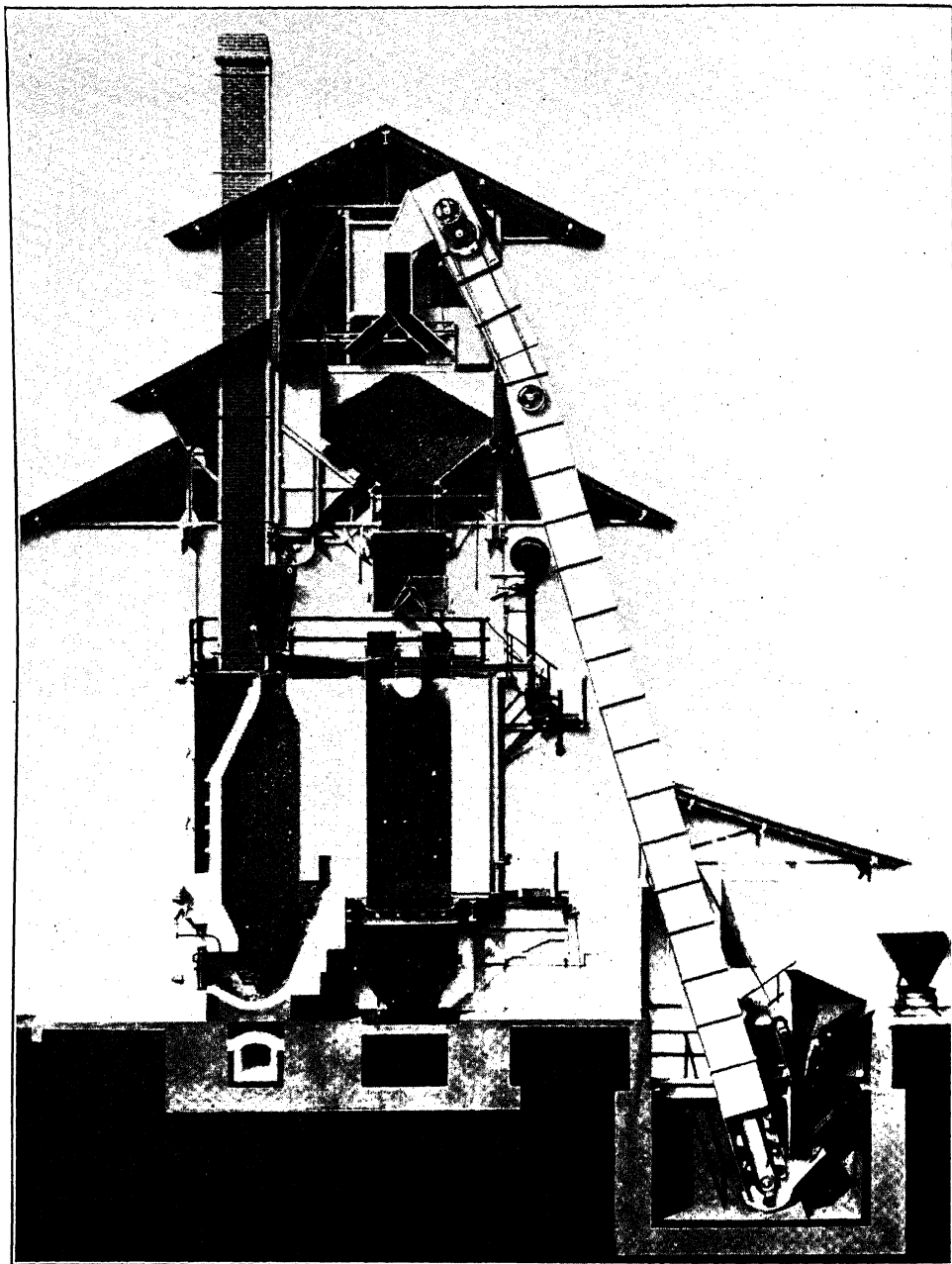
The ovens have been built here in two sizes, the larger holding 4 tons of coal per charge, and the smaller $1\frac{3}{4}$ tons. They are built of interlocking sectional silica tilework with self-sealing charging and discharging doors. In the larger size the lower doors are operated hydraulically, and the charging larry and hot coke car are operated by electric power.

The heating of the ovens is done by hot producer gas made from coke and breeze, and the waste heat is used to heat the secondary air for combustion. The heating gases enter adjacent to the bottom of the ovens and leave at the top. One of the characteristics of this type of oven is that, on account of the taper of the ovens, a lower temperature suffices at the top to complete the coking in the proper period as compared to the heat required at the base. For this reason the waste gases enter the waste heat recuperators at a lower temperature than in other oven construction. This conduces to fuel economy, and, in fact, in heating requirements these ovens compare favorably with larger installations of other types. The ovens are built in settings of four to six ovens with division walls separating each setting—a construction that permits intermediate settings to be rebuilt without taking the other settings out of service.

The smaller ovens are heated from built-in hand-clinkered producers arranged one producer to each setting, or group of four to six ovens. The larger ovens are heated by producer gas generated in central producers of the self-clinkering type, which burn breeze and small coke mixtures and thus increase the amount of salable coke.

One of the most important characteristics of the intermittent vertical oven is its adaptability to "steaming." In this process steam is admitted to the bottom of the oven, towards the end of the carbonization period. The steam displaces the residual coal gas and produces water gas in combination with the hot coke charge. The result is a material increase in the yield of gas, and by regulating the amount of steaming the calorific value of the gas can be closely controlled. It likewise tends to prevent the growth of graphitic carbon deposits on the wall which otherwise would cause considerable lost time in operation. Coke produced with steaming shows no deleterious effect in comparison with coke produced without steaming. The slight film of ash which might form on the surface of the coke is shaken off in discharging and handling and is lost in the breeze or screenings. The production of water gas by steaming is relatively economical. Since radiation and other losses are not increased, the water-gas generation may be viewed as at marginal cost. Moreover, the detrimental side-wall carbon is in large part converted into useful gaseous heat.

Vertical ovens are generally installed in gas plants where nut or slack high-volatile coal is carbonized and the coke is sold for domestic purposes. The coke is blocky, reactive, and well adapted to domestic use. In one plant, pulverizing the coal gave good results. Some typical operating results are shown in Table II.



*Courtesy of The U. G. I. Contracting Company, Division of
United Engineers & Constructors, Inc., Philadelphia, Pa.*

FIG. 21. The U. G. I. intermittent chamber oven.

TABLE II

OPERATING RESULTS, INTERMITTENT VERTICAL CHAMBER OVENS * USING HIGH-VOLATILE GAS COAL

	Plant A	Plant B	Plant C
Volatile-matter content of coal, percent dry ash-free	37.5	35.0	37.5
Coal charge, pounds	3,800	8,494	3,800
Coking time, hours	12	12	12
Steaming time (included in coking time), hours	3	3	3
Steam, percent of coal	2.6	7.7	4.0
Gas yield, cubic feet per pound dry coal	6.44	7.67	6.85
Btu of gas per cubic foot	560	524	543
Btu of gas per pound dry coal	3,606	4,015	3,721
Coke yield, dry, percent	68.0		
Producer fuel, dry, pounds per ton coal	238	329 †	257
Producer fuel, combustible, pounds per ton coal	225	272	242
Gas composition, percent			
Carbon dioxide	2.1	3.4	
Illuminants	3.4	2.0	
Oxygen	0.4	0.3	
Carbon monoxide	13.5	16.5	
Hydrogen	51.9	53.9	
Methane	24.3	22.7	
Nitrogen	4.4	1.2	
Total	100.0	100.0	
Specific gravity (air = 1.0)	0.447	0.461	
Hydrogen sulfide (grains per 100 cubic feet)	95	340	
Coke shatter test:			
Percent over 2 inches	44.6		
Percent through ¼ inch	13.2		

* Actual plant data, submitted by United Engineers and Constructors, Inc., Philadelphia, for three plants, over a period of thirty days or more; Plants A and C, small ovens, Plant B, large ovens.

† Half coke and half breeze.

CONTINUOUS RETORTS

The continuous retort represents a development to give a minimum-labor carbonization unit for carbonizing 40 to 100 tons of coal per day. One of the most recent units developed is that invented by van Ackeren.¹⁹ Coal is fed continuously

to the retort, and coke is removed continuously at the bottom.

Figure 22 gives an excellent view of the continuous vertical combination (heated either with oven gas or producer gas) ovens at Sterling, Ill. Figures 23 and 24 show the method of feeding coal and of extracting the coke, as well as adjacent heating walls.

Few vertical continuous plants are now built in America and it is doubtful that this type of construction will revive until natural gas has been dissipated, requiring the construction of small carbonization plants.

SOLE-HEATED OVENS²⁰

This type of oven was first used in America for the production of a dense, low-volatile petroleum coke from petroleum residues. It was subsequently adapted to the carbonization of coal. As can be seen from Fig. 24,¹⁵ all the heat comes from beneath the coal through the top of the sole flues in which the gas burns.

The coking rate is quite high, as much as 0.8 inch per hour being claimed. The rapid coking of certain types of coal, particularly the high-oxygen coals,²¹ has been noted as beneficial. Whether or not this is true, the Curran-Knowles oven lends itself well to the carbonization of such Illinois coals as have been tried in these ovens. However, it must not be overlooked that previous oven builders, such as Roberts,²² claimed that special types of ovens had to be used to carbonize Illinois coals. These statements were refuted in tests at St. Paul, Minn., using coke ovens

²⁰ Thiessen, G., *Ind. Eng. Chem.*, **29**, 506-13 (1937). Stevenson, W. W., *Am. Gas J.*, **148**, No. 2, 9-13 (1938). Given, I. A., *Coal Age*, **45**, No. 5, 33-5 (1940).

²¹ Ovitz, F. K., *U. S. Bur. Mines, Bull.* **135** (1917), 71 pp.

²² Roberts, A., *U. S. Pat.* 1,352,696 (1920).

¹⁹ Van Ackeren, J., *U. S. Pats.* 1,704,685-7 (1929).

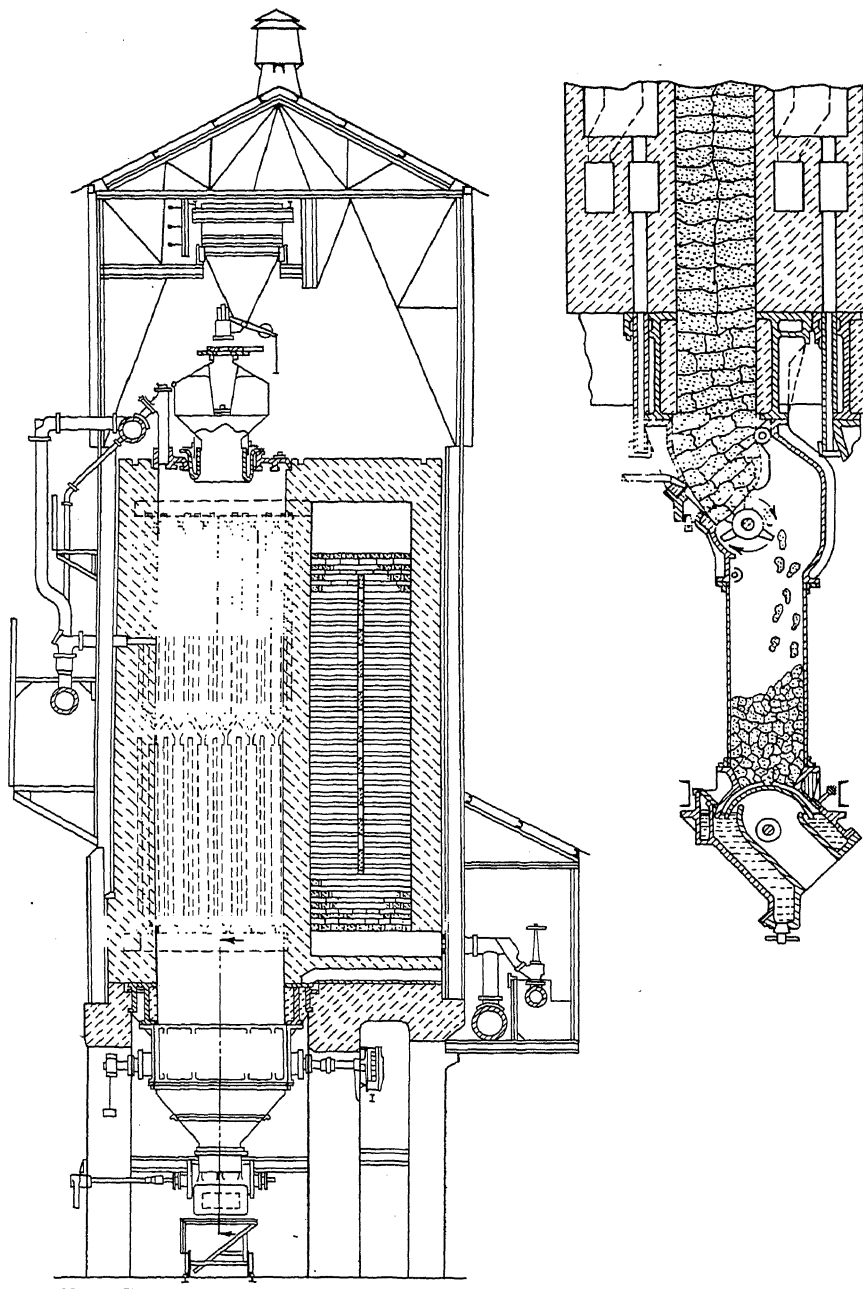


FIG. 22. Koppers-van Ackeren continuous vertical oven with side view of coke removal.

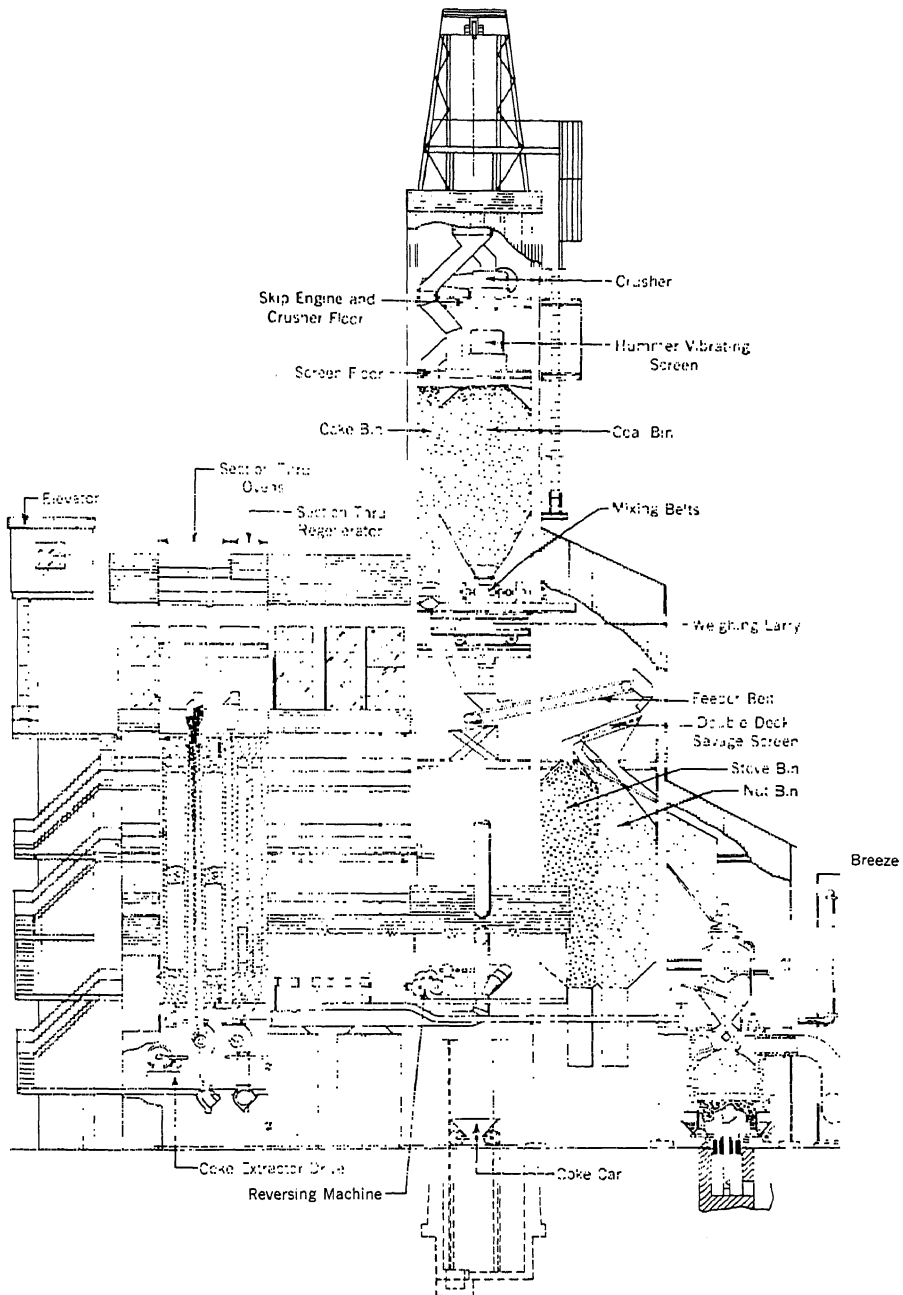


FIG. 23. Sectional view of Koppers-van Akeren continuous vertical oven.

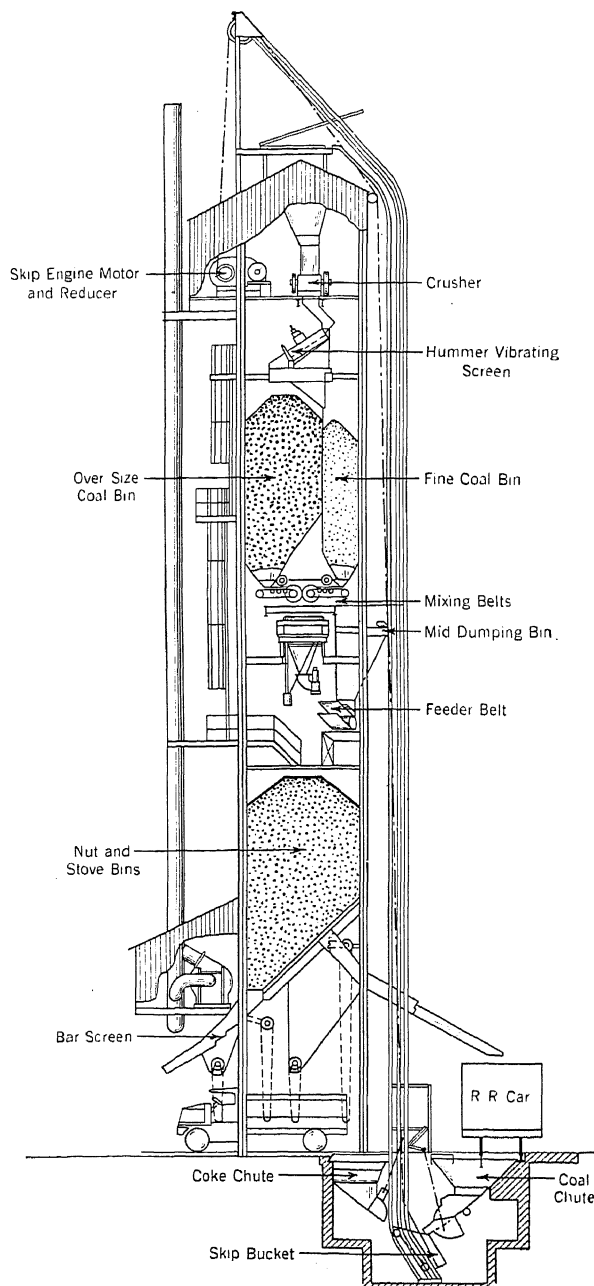


FIG. 24. Coal and coke bins used with Koppers-van Akeren continuous vertical oven.

of ordinary type.²³ The principle of the sole-heated oven is shown in Fig. 25.

ELECTRICALLY HEATED OVENS

A very ingenious scheme of coal carbonization was devised by Stevens.²⁴ The process is intermittent and can be made continuous. (See Fig. 26.) A column of

Though technically ingenious, the process must compete for gas-manufacturing purposes with the regular byproduct oven underfired with producer gas. The following simple calculation will demonstrate this.

One ton of coal requires 400 kilowatt-hours for carbonization by the Stevens process.

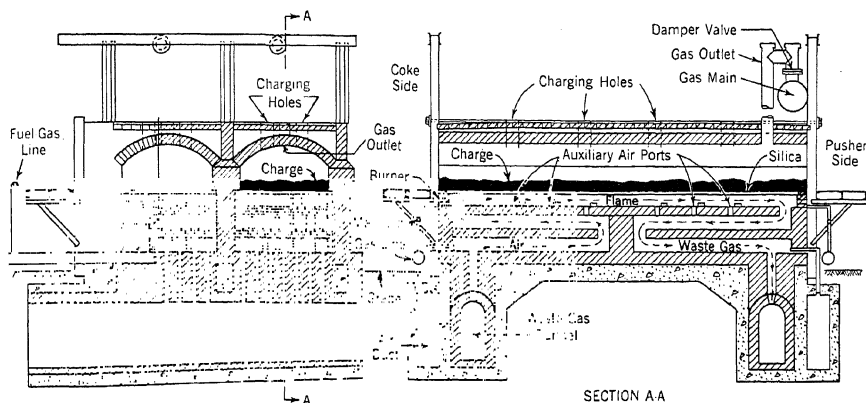


Fig. 25. Sections through Knowles sole-flue ovens.

coke breeze is set up in a suitable container, surrounded with coal, and electricity is passed through the breeze, thus heating the breeze and carbonizing the surrounding coal. When the adjacent coal has been carbonized it becomes a relatively good conductor, thus progressively heating adjacent coal, and the path of the electrical flow becomes larger. The rate of carbonization is fast, as high as 4 inches per hour being claimed. The power consumed runs from 350 to 400 kilowatt-hours per ton of coal.

²³ McBride, R. S., and Selvig, W. A., *Natl. Bur. Standards (U. S.), Technol. Paper* **137** (1919), 51 pp.

²⁴ Stevens, H., *Proc. Fuel Engrs. Conf., Appalachian Coals, Inc.*, **3**, 412-41 (1936); *Trans. Electrochem. Soc.*, **75**, 167-83 (1939). Curtis, H. A., Stitzer, Ralph B., and Darby, W. J., *Ind. Eng. Chem.*, **32**, 757-62 (1940).

One ton of coal requires 250 pounds of coke to make producer gas.

With coke worth \$6.00 per ton, \$1.00 per ton capital charge for the producer, and \$1.00 per ton (high) operating cost of producers, the cost of producer underfiring will be

$$\frac{250}{2,000} \times \$8 = \$1.00$$

Power would have to be furnished to an electrically heated plant at a price of $\frac{100}{400} = \frac{1}{4}$ cent per kilowatt-hour to compete with such practice. Where the power can be furnished at $\frac{1}{4}$ cent per kilowatt-hour the electrical process is competitive; if under $\frac{1}{4}$ cent, the electrical process could replace the older producer-fired methods. If the process must depend on cheap off-

mass caused by the slow heat transmission through coal mass; (3) the short life of the metal vessels in which coal is held and coked; and (4) the high cost of investment in static processes. Briefly summarized, these mechanical difficulties have slowed down the development of low-temperature carbonization.

Low-temperature char may, perhaps, find a use as a "filler" for certain high-volatile coals that are carbonized at high temperatures. It is a well-known fact that the addition of low-volatile to high-volatile coals greatly improves the resultant coke when the mixture is coked at high temperatures. However, it is uneconomical in certain localities to ship low-volatile coal to the high-temperature coke plants. Unpublished experiments made since the first World War at the plants of several large high-tempera-

ture coking units have demonstrated the value of adding low-temperature char containing 15 to 18 percent volatile matter to the high-volatile coal to be coked. The results upon adding about 15 percent by weight of low-temperature char compare favorably with those obtained by the addition of a slightly lower amount of low-volatile coal. In order that this practice may develop it will be necessary to devise a satisfactory method of making the desired char.

The most satisfactory American method is the Wisner process as developed and modified by the Pittsburgh Coal Company.²⁹ More than ten years of effort has been expended, and the present plant produces 7,000 tons of low-temperature coke per month. The process is continuous; it is illustrated by Fig. 27, and the general di-

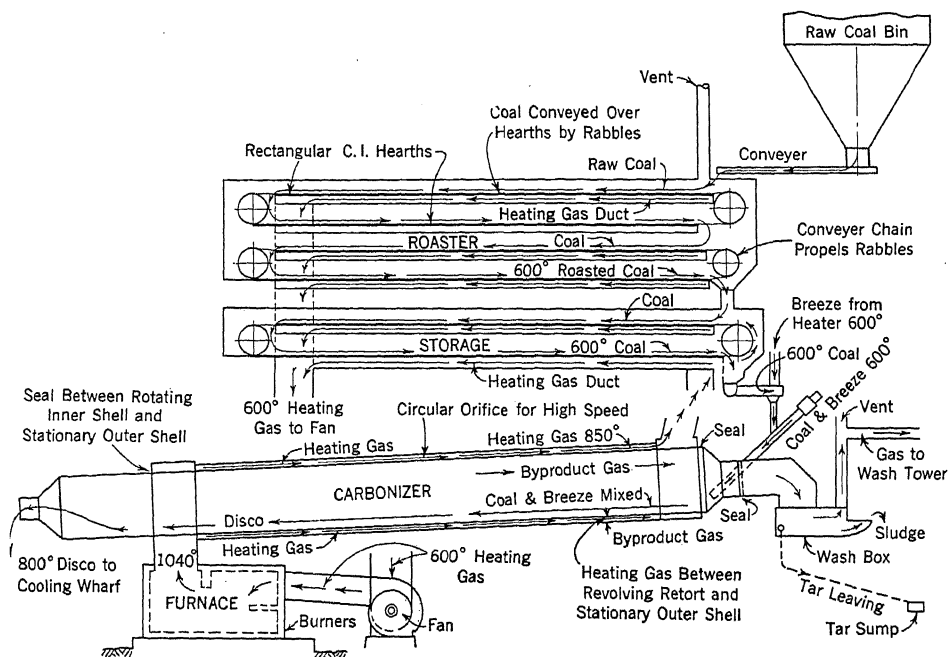


FIG. 27. Flow diagram of low-temperature coking unit, using Disco process, for strongly coking coals.²⁹ (Temperatures in degrees Fahrenheit.)

mensions of the units of the plant at Champion, Pa., are given in Table III.

Coal is fed from storage bins into roasters, where the coal is heated to 600° F and oxidized by means of the hot gas previously circulated about the carbonizer. The coal passes into the rotating carbonizers, which are inclined, rotating steel cylinders. Surrounding the rotary cylinder is a stationary shell insulated on the outside. Heating gases pass through the annular space be-

tween the two shells at high speed and heat the revolving element. Byproduct gas is withdrawn from the upper end of the cylinder by an exhauster. As the oxidized coal is fed to the carbonizer cylinder, a definite proportion of breeze is added. The mixture is carried down the inclined retort and carbonized into coke balls during its traverse thereof. The coke is discharged from the lower end of the retort to the atmosphere. It is claimed that 85 percent of the

TABLE III

DIMENSIONS OF CARBONIZING UNITS AND OPERATING DATA OF THE PITTSBURGH COAL CARBONIZATION COMPANY ²⁹

Item	Unit 1	Unit 2	Unit 3
Diameter	6 ft	8 ft	8 ft
Length overall, cold	91 ft 3½ in.	106 ft 10 in.	126 ft 10 in.
Center-line tires (cold)	54 ft	84 ft 10 in.	104 ft 6 in.
Slope	½ in. in 12 in.	⅜ in. in 12 in.	¼ in. in 12 in.
Total rotating weight, pounds	110,000	106,900	138,000
Motor horsepower	30	30	50
Speed, rpm	900	720	900
Horsepower used	19-21	16	21-23
Carbonizer, rpm	5.25	3.44	2.89
Maximum expansion, inches	3½	5⅞	6⅞
Center-line hoods	76 ft	71 ft 3 in.	90 ft 9 in.
High-speed heat area, square feet	1,432	1,791	2,306
Feed raw coal per hour, pounds	6,250	9,580	12,330
Feed breeze per hour, pounds	1,875	2,875	3,700
Total feed per hour, pounds	8,125	12,455	16,030
High-speed heating area, pounds per hour per square foot	5.67	6.95	6.95
Heating gas, pounds per minute	825	1,059	1,304
Feed, pounds per pound heating gas	0.164	0.196	0.205
Heating gas at 700° F, cubic feet per minute	25,000	32,000	39,500
Combustion air blower, cubic feet per minute	1,680	2,300	2,300
British thermal units per hour	4,356,000	5,592,000	6,904,000
Tons coal per 24 hours	75	115	148
Size heating gas fan, inches	42 by 12	48 by 15	54 by 18
Fan motor, horsepower	25	25	20-30
Speed, rpm	720	600	450 *
Horsepower used	20	21	28
Roaster-hearth area, square feet	1,200	1,955	1,955
Storage capacity, hours	1-3	1-3	1-3

* Rewound 30-horsepower, 600-rpm motor.

gas made is used for heating. The yield of products per 2,000 pounds of coal charged is as follows:

PRODUCT	WEIGHT PERCENT	PER TON COAL
Coke	72.00	1,440 pounds
Gas	12.50	3,720 cubic feet
Tar	7.50	15.8 gallons
Light oil	0.78	2.5 gallons
Liquor	5.49	6.6 gallons
Loss	5.60	
<hr/>		
103.87		

MATERIALS OF CONSTRUCTION FOR COKE OVENS

The coke-oven chamber walls, combustion flues, and the regenerator walls which support them are of silica brick. Silica brick is made from crushed quartzite bonded with 2 percent of lime. The quartzite is very pure, and the rock selected must contain 98 percent silica. In contrast with clay brick, which have a glassy bond, silica brick are bonded by recrystallized modifications of quartz. Fireclay brick was used in oven construction in continental Europe before the first byproduct coke ovens of silica construction were built at Joliet, Ill., in 1909. American genius was responsible for the placement of silica brick in the Joliet batteries. Despite the fact that silica brick expands more than fireclay brick, the Joliet ovens showed that silica brick were practical. In addition, higher coking rates could be attained because flue temperatures could be higher and also because silica brick conducts heat more rapidly than fireclay brick at the same temperature. European oven constructors were hesitant to adopt what they considered to be a radical departure, and in England silica brick was not used extensively until about 1925.

A good many silica-brick coke-oven batteries have been operated safely at flue

temperatures of 2,600 to 2,700° F; when clay-brick ovens are thus operated, the oven walls sag and distort owing both to the formation of excessive amounts of glass and to the bearing pressures incident to oven construction. Silica brick on the other hand do not soften at such temperatures but melt abruptly at a temperature in excess of 3,000° F.

The anomalous thermal-expansion characteristics of silica brick and its low price are important factors in making it well suited for coke-oven construction. Figure 28 presents thermal-expansion curves for clay and silica brick and the crystalline modifications of silica: quartz, cristobalite, and tridymite.

It can be seen from the figure that, although fireclay brick expands less than silica brick at temperatures up to 1,000° F, at about 1,600° F the silica brick curve is practically parallel to the temperature axis while the fireclay brick continues to expand. Since oven wall masonry is usually in a temperature range above 1,600° F, little change in length occurs in normal service; this statement is true only if the silica brick have been previously well fired to insure a minimum amount of residual quartz in the fired product.

The high-temperature load-bearing property of silica brick is a major contribution to its value in coke-oven service. As a result of their crystalline bond, silica brick will support a load of 25 pounds per square inch at a temperature of 2,900° F, which is fairly close to their melting point (about 3,000° F). Fireclay brick, however, when subjected to a short-time load test of 25 pounds per square inch, show an appreciable sag or subsidence at 2,450° F. Furthermore, fireclay will fail completely under a load of 25 pounds per square inch at a temperature of 2,200 to 2,300° F in a long-time test. Figure 29 shows crushing

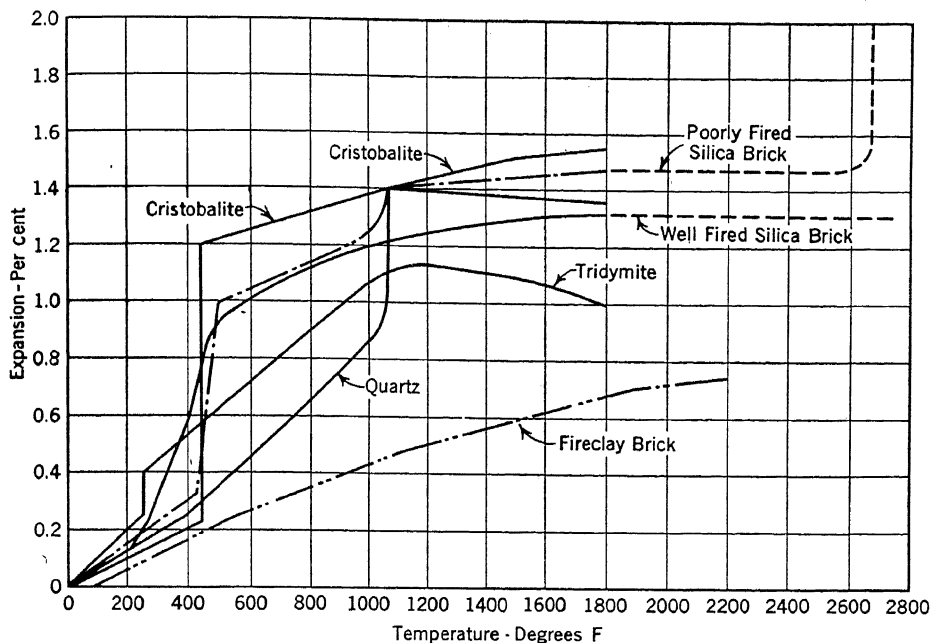


FIG. 28. Reversible thermal expansion of clay and silica brick.

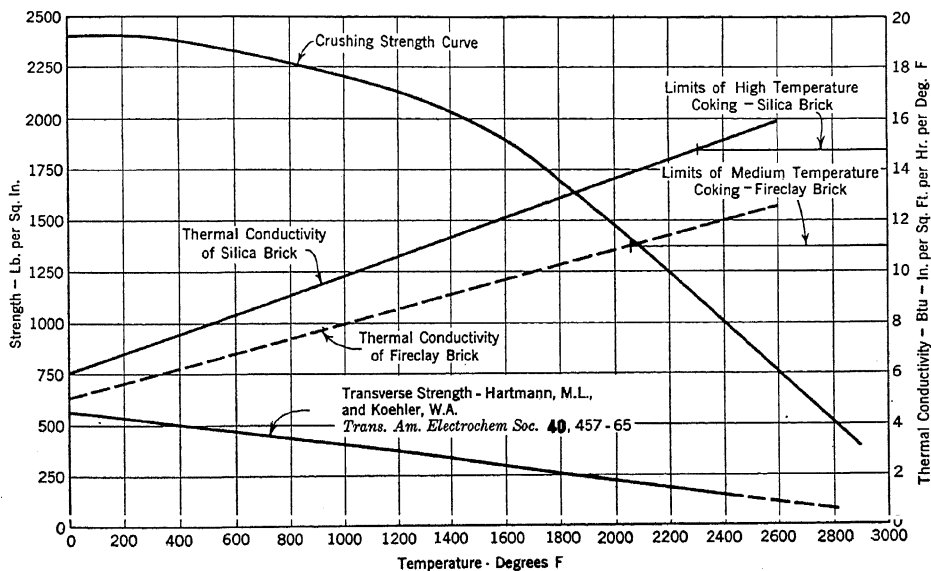


FIG. 29. Strength of silica brick at elevated temperatures and thermal-conductivity values for silica and fireclay brick at various temperatures.

strength-temperature relations for fireclay and silica brick. A vertical cross section through an oven with bearing loads and temperature ranges encountered at various points has been prepared in Fig. 30. The data presented in these figures show why silica brick is particularly valuable for ovens to be operated at high coking rates.

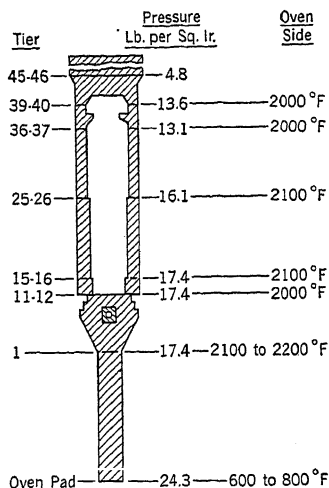


FIG. 30. Stresses and temperatures at various levels in a modern byproduct coke oven.

A comparison of byproduct coke ovens with other high-temperature furnaces in use in metallurgical plants indicates that coke ovens are the largest units in size and mass of masonry, and yet their heating up and operation have been so highly perfected that they have the best service record in terms of life and tonnage throughput. Twenty years of useful life have been recorded for many coke-oven batteries, and in that time a battery of fifty ovens may have carbonized from 5 to 9 million tons of coal.

HEAT OF CARBONIZATION

The amount of heat required to carbonize coal is important in many respects. This

heat represents fuel that might be usefully utilized for other purposes, and, of course, this fuel has a high economic value. In Fig. 31 the cost of underfiring a ton of coal using 550-Btu coke-oven gas is shown. When using gas valued at 25 cents per 1,000 cubic feet with an underfiring requirement of 1,100 Btu per pound, the heating cost amounts to \$1.00 per ton of coal; with 10-cent gas the cost is 40 cents per ton of coal. The economic value of the fuel consumed demands that the subject of underfiring be seriously considered; in fact, it is one of the principal considerations of design. All the larger modern coking units are designed with regenerative systems of

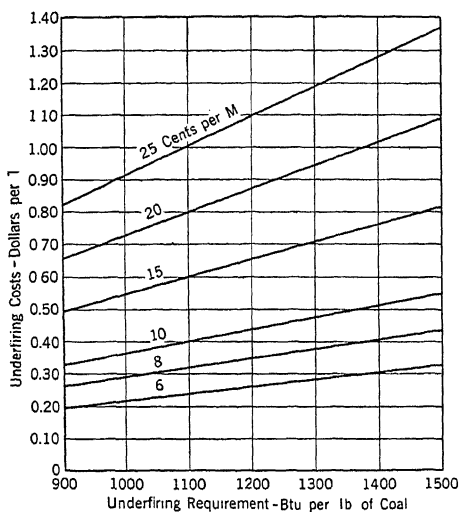


FIG. 31. Relation between underfiring requirement and underfiring cost per ton of coal using oven gas of 550 Btu per cubic foot.

heating. The flues, mixing ports, and waste-gas systems are designed to secure uniformly graded heating from end to end and from top to bottom of the coke oven. Many schemes of gas and air mixing have been tried, and this particular phase of the art is in a constant state of flux. Every attempt is made by designers and operators

to reduce the underfiring requirements. Figure 32 shows the large amount of money that can be saved yearly, assuming various Btu savings per pound of coal. For example, a saving of 100 Btu per pound of coal in gas (550 Btu) valued at 15 cents per

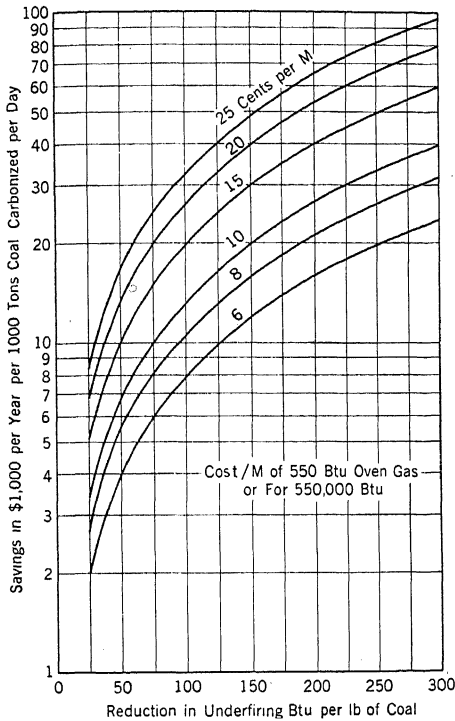


FIG. 32. Savings possible from various reductions in underfire rate.

1,000 cubic feet will amount to \$20,000 per year for a plant carbonizing 1,000 tons of coal per day. Of course, before economic savings can be made, technical excellence in distribution of the heat must be assured.

The principal losses of heat from a coke oven are:

1. Radiation and convection from the outside surface. This is a function: (1) of the material of construction of the outside surface, such as cast iron, clay brick, glazed

brick; (2) of the temperature of the exposed brickwork, which in turn depends on the temperature of the adjoining brickwork; (3) of the wind velocity; and (4) of the weather; etc.

2. Temperature of coke as pushed. For example, see Fig. 33, which shows the sensible heat content per pound of coke as pushed at various temperatures for an average American coke. Assuming the coke to be pushed at 1,800 and 1,900° F, there will be a difference in sensible heat of about

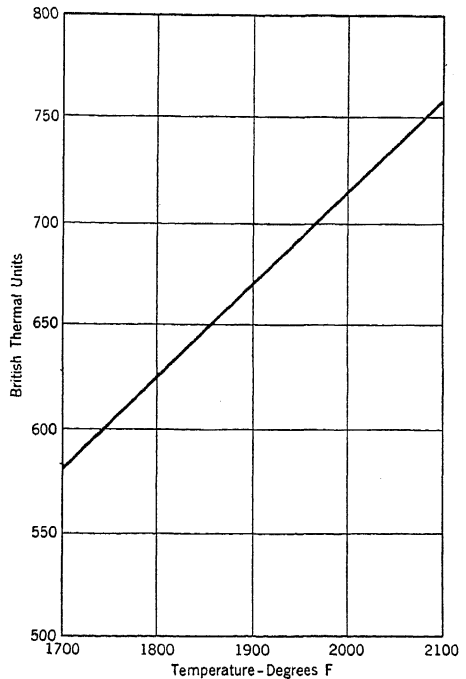


FIG. 33. Heat content per pound of average American coke.

45 Btu per pound of coke. If the burning system operates at an efficiency of 60 percent, which is a fair practical average, then the total heat required would amount to $45/0.60 = 75$ Btu additional heat required per pound of coke, exclusive of higher

losses due to higher temperature of the gaseous products of distillation. If the coke yield per pound of coal amounts to 70 percent, then the total additional heat required per pound of coal will be 75×0.7 , or 52.5 Btu per pound of coal. This one fact has been overlooked by coke-plant operators more than any other factor with re-

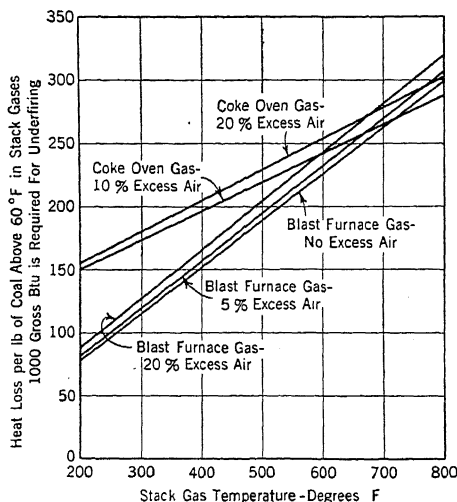


Fig. 34. Heat content of waste gas.

spect to underfiring economy. Some plants follow the practice of annealing the coke at the end of the coking period in order to harden the coke and improve its physical properties. It is obvious that such practice is heat consuming and raises the underfiring.

3. Various handbooks cite ample data as to stack losses. These losses entail the sensible heat carried out by the stack, and they are a function of regenerator efficiency, amount of excess air used, and temperature and water saturation of the fuel gas and air. Figure 34 shows the losses when burning various gases.

4. Heat carried out by products distilled from the coking chambers is illustrated in

Fig. 35. Little can be done to reduce this item in practice. It is, of course, a function of the temperature of coking, which in turn is controlled by the desired end temperature of the coke and the rate of coking. One important controllable factor in standpipe or foul gas loss is the loss due to evaporation of free moisture on the coal as illustrated in Fig. 36. The heat involved is the sum total of the latent heat of the moisture plus the sensible heat to raise the steam to standpipe temperature and is a considerable factor. It has been argued that not all this heat is abstracted from the heating system, but rather that the hot gases formed on carbonization evaporate and heat up the free water, the net effect being merely to reduce the temperature of the standpipe gases. However, most practical operators agree that added moisture to coal raises underfiring requirements. The various arguments on this point are covered in Chapter 23.

All the above heat requirements are summarized in heat balances. Unfortunately, few good coke-oven heat balances have been published, particularly for American practice. The Germans have carried out some very thorough work through various cooperative testing organizations. Baum³⁰ and others have discussed heat balances and many phases of coke-plant fuel economy. Other German writers, among them Senfter, Rummel, Littscheidt, and Terres, and American workers like Munster and Davis have also studied the problem carefully.³¹

³⁰ Chapman, W. R., *Fuel*, 5, 355-61 (1926). Burke, S. P., and Parry, V. F., *Ind. Eng. Chem.*, 19, 15-20 (1927). Burke, S. P., Parry, V. F., and Schumann, T. E. W., *Proc. Am. Gas Assoc.*, 1930, 820-55; *Fuel*, 10, 148-71 (1931). Baum, K., *Arch. Eisenhüttenw.*, 2, 779-94 (1929); *Glückauf*, 66, 185-91 (1930); *Proc. 3rd Intern. Conf. Bituminous Coal*, 1, 507-39 (1931). Baum, K., and Littscheidt, W., *Brennstoff-Chem.*, 13, 386-91 (1932).

³¹ Hollings, H., and Cobb, J. W., *J. Chem. Soc.*, 107, 1106-15 (1915). Mezger, R., and

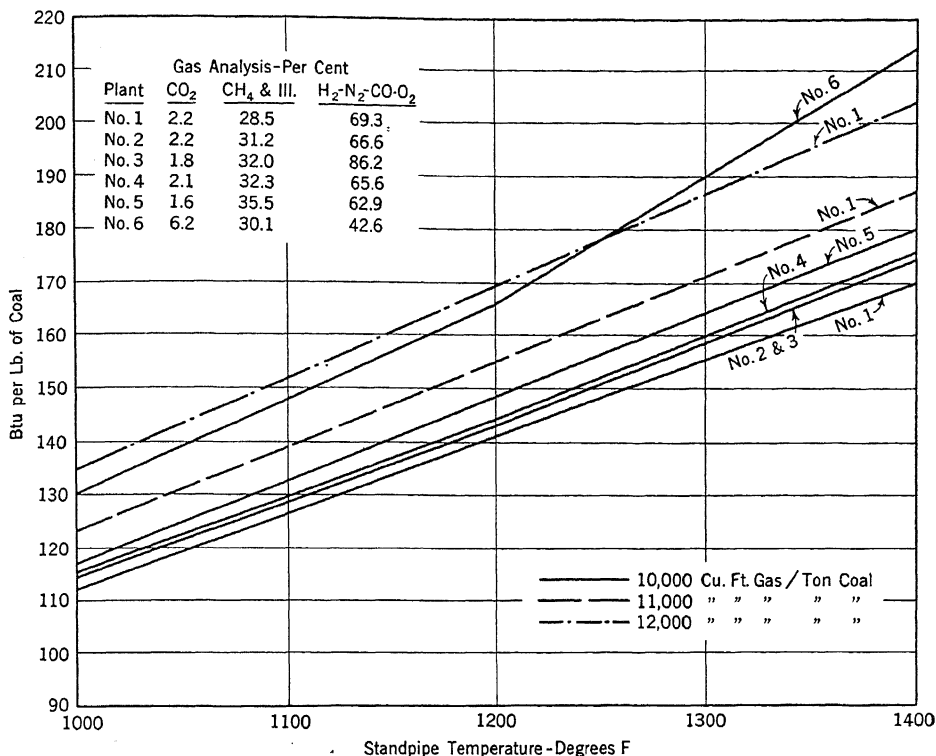


Fig. 35. Heat carried out of ovens by products of distillation as a function of the standpipe temperature.

Coke-oven people have not followed up as vigorously as possible heat balances and the lessons they teach. The electric-power industry has been much more alive to such studies with respect to boiler operation, and

the study of such heat balances has been of material assistance in improving fuel consumption per kilowatt-hour of power generated. Coke-oven heat balances should be made by all operating plants whether new

Müller, M., *J. Gasbeleucht.*, **63**, 669-73 (1920). Grau, H., *Brennstoff-Chem.*, **2**, 97-9 (1921). Strache, H., and Grau, H., *ibid.*, **2**, 97-9 (1921). Sieben, K., *ibid.*, **3**, 209-11 (1922). Strache, H., and Frohn, E., *ibid.*, **3**, 337-40 (1922). Munster, J. K., *Blast Furnace Steel Plant*, **11**, 389-92 (1923). Davis, J. D., and Place, P. B., *Ind. Eng. Chem.*, **16**, 589-92, 726-30 (1924). Davis, J. D., Place, P. B., and Edeburn, P., *Fuel*, **4**, 286-99 (1925). Winter, H., *Brennstoff-Chem.*, **7**, 117-23 (1926). Terres, E., and Wolter, H., *Gas- u. Wasserfach*, **70**, 30-4, 53-8, 81-5 (1927). Terres, E., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 657-84

(1928). Terres, E., and Meir, M., *Gas- u. Wasserfach*, **71**, 457-61, 490-5, 519-23 (1928). Terres, E., *ibid.*, **72**, 361-9 (1929). Terres, E., and Voituret, K., *ibid.*, **74**, 97-101, 122-8, 148-54, 178-83 (1931). Terres, E., Tjia, H. A., Herrmann, W., Johswich, F., Patscheke, G., Pfeiffer J., and Schwarzmann, H., *Angew. Chem.*, **48**, 17-21 (1935). Féodoroff, V., *Chimie & industrie*, **22**, 231-48 (1929). Dubois, J., *Gas i Woda*, **11**, 313-7 (1931). Niemann, P., *Brennstoff-Chem.*, **12**, 386-9 (1931). Litterscheidt, W., *Glückauf*, **70**, 77-84, 106-12 (1934), **71**, 173-81 (1935). Norkin, N. N., *Coke and Chem. (U.S.S.R.)*, **7**, No. 10, 16-24 (1937). Senfter, E., *Arch. Eisenhüttenw.*, **13**, 1-14 (1939).

or old so as to indicate to operators possible savings in fuel.

Before delving into actual heat balances it is well to point out that it is German practice to report underfiring practice in

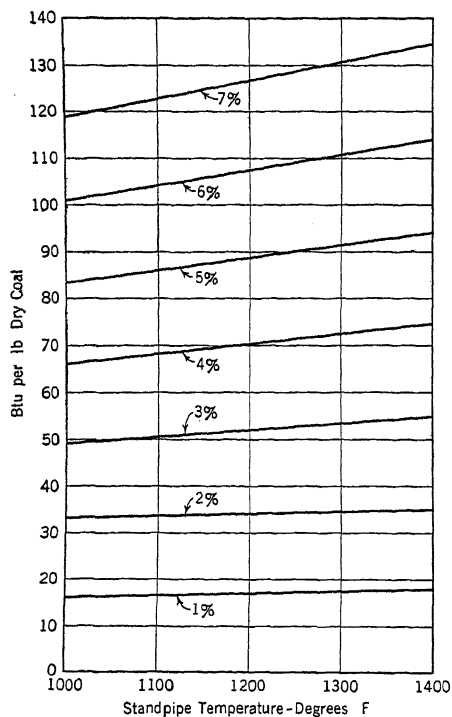


FIG. 36. Effect of free moisture content of the coal on the amount of heat carried out of the ovens as a function of the standpipe temperature.

terms of *net* heating value of gas, whereas it is American practice to report values in *gross* heating value. This often makes comparisons between German and American practice difficult. For example, in Table IV a typical American heating gas has a gross heating value of 572 Btu and a net heating value of 512 Btu. If 2 cubic feet of this gas is required per pound of coal the difference in reported values between gross and net heating values will be $2 (572 - 512) =$

120 Btu. If the reader will bear this figure in mind when comparing reported German figures with American figures, much confusion will be eliminated.

A typical German study leading to the determination of the exothermic heat of coking is that of Senfter.³¹ The figures have been converted to Btu for convenience (Table V). A wide variation of heat input may be noted, and a wide variation is shown in the exothermic heat. It is to be borne in mind that each test represents a different coal, although all are Saar Valley coals. The average exothermic heat in these six tests was 202 Btu per pound of coal. A similar American table is set up for two different American plants: the first for a modern (1939) Becker battery heated by blast-furnace gas, the second, for a Koppers battery (test in 1922) heated with coke-oven gas (Table VI). In the first plant there was an exothermic heat of 195 Btu and in the second one of 206.4 Btu, or a mean value of 201 Btu, which is in surprisingly good agreement with the German values as shown in the above test. A complete heat balance of the same two American plants exhibits a remarkable agreement per pound of coal (Table VII).

The efficiency³² of the two American

³² Efficiency is defined as

$$\frac{\text{Sensible heat in products of distillation}}{\text{Heat input}}$$

This definition neglects exothermic heat and, in fact, takes advantage of exothermic heat to show a high efficiency. For example, on this basis the efficiency of the blast-furnace heated unit is 78.1 percent, whereas on a basis of

$$\begin{aligned} \text{Efficiency} &= \frac{\text{Input} - \text{Stack losses} - \text{Radiation, etc.}}{\text{Input}} \\ &= \frac{1,040 - 226.7 - 195.4}{1,040} = 59.5 \text{ percent} \end{aligned}$$

or efficiency based on input + exothermic heat less stack and radiation losses *versus* sum total heat input by fuel gas + exothermic heat:

$$\frac{1,234.9 - 226.7 - 195.4}{1,234.9}$$

TABLE IV

COMBUSTION DATA ON DRY COKE-OVEN GAS

Component Gases	Cubic Feet per Cubic Foot of Fuel Gas	Gross Heating Value, Btu per Cubic Foot, Saturated	Net Heating Value, Btu per Cubic Foot, Saturated	Actual Gross Heat Liberated, Btu per Cubic Foot of Fuel Gas	Actual Net Heat Liberated, Btu per Cubic Foot of Fuel Gas
CO ₂	0.0220	0	0	0	0
O ₂	.0080	0	0	0	0
N ₂	.0810	0	0	0	0
CO	.0630	321.7	321.7	20.27	20.27
H ₂	.4650	325.0	274.6	151.13	127.69
CH ₄	.3210	1015	914	325.82	293.39
C ₂ H ₄	.0350	1615	1514	56.53	52.99
C ₆ H ₆	.0050	3758	3607	18.79	18.04
Totals	1.0000			572.54	512.38

The theoretical volume of air required for perfect combustion will be 4.9571 cubic feet of dry air per cubic foot of dry gas.

TABLE V

DETERMINATION OF EXOTHERMIC HEAT OF COKING BY SENFTER ³¹

Battery	B	C	D	F	G	K
Temperature of coke as pushed, °F	1,832 *	1,796	1,967	1,648	1,985 †	1,942
Temperature of gases as distilled, °F	1,220	1,148 ‡	1,458	1,023	1,571 †	1,404
Sensible heat of coke	470 ‡	457	535	414	534	522
Sensible heat of tar, benzol, and nitrogen	32	31	34	34	40	34
Sensible heat of gases	180	167	213	140	250	202
Water and unaccounted	20	18	31	14	45	43
Total sensible heat	702	673	813	602	869	801
Ash content of dry coke, percent	7.9	7.9	7.5	4.3	7.6	7.55
Sensible heat of ash	36	36	38	20	40	38
Sensible heat due to pure coal substance	647	619	752	578	803	750
Total sensible heat	683	655	790	593	843	788
Heat of underfiring §	473	477	624	498	567	503
Exothermic heat of dry coal	210	178	166	95	276	285
Exothermic heat of pure coal	228	196	180	103 ¶	297	294

* Estimated.

† Overcooked.

‡ Included battery C, because of almost identical coals.

§ This figure must be total underfiring less sum of stack losses, radiation, etc.

|| On account of Goldsmith flue and of positive heat of cracking.

¶ Especially low owing to use of Baesweiler coals.

TABLE VI

HEAT BALANCE OF COMBUSTION FOR OVEN HEATING PER POUND OF COAL

	Dr. W. C. Rueckel, Tests for Koppers Company Blast Furnace Gas Un- derfiring		J. K. Munster ³¹	
Sensible heat introduced, Btu				
By coal	1		1.6	
By air	
By fuel gas	1		1.4	
By combustion fuel gas	1,038		1,344.6	
Total	1,040		1,347.6	
Sensible heat in products, Btu				
In coke	(1,945° F)	484.6	(2,000° F)	552
In gas yield		158.6		195
In water vapor	(1,220° F)	128.9	(1,200° F)	130.5
In tar and light oil		40.7		8.5
In stack gas	(515° F)	226.7	(650° F)	490
In radiation and convection		195.4		178
Total		1,234.9		1,554.0
Exothermic heat of carbonization, Btu		195		206.4

units is:

$$\text{Blast-furnace-gas heating} \quad \frac{812.8}{1,040} = 78.1 \text{ percent}$$

$$\text{Coke-oven-gas heating} \quad \frac{1,347.6}{1,347.6} = 65.8 \text{ percent}$$

Baum in his article in the *Proceedings of the Third International Conference on Bituminous Coal*³⁰ showed a table claiming 68.3 to 78 percent technical furnace efficiency. Thus, it can be seen on this basis that American ovens are equal in efficiency to German ovens.

It is a moot question whether there is any exothermic heat. Terres and Davis³¹ both showed that if there is any at all it is quite small, of the order of 40 Btu per pound of coal. Terres, by means of an interesting curve (Fig. 37, which is converted to a Btu basis for the American reader) in

both his German and American papers, showed the variation of the endothermic and exothermic heat with the heat of carbonization for a number of German coals. Both Terres and Davis carried on very careful laboratory work and obtained much lower exothermic heats than is indicated by the above heat balances based on large-scale operations. It is admittedly difficult to collect sufficiently accurate data on large tests, but nevertheless results of various large-scale tests show values in the neighborhood of 200 Btu per pound exothermic heat. The error in these tests is of the order of 4 or 5 percent. The difference between Terres' and Davis' 40 to 50 Btu and practical tests of 200 Btu is too large to be attributed to faulty methods of measurement. There is one possible explanation for the appearance of a large exothermic

TABLE VII

HEAT BALANCE OF CARBONIZATION PROCESS,
INCLUDING COMBUSTION FOR OVEN HEATING
PER POUND OF COAL

	Dr. W. C. Rueckel, Tests for Koppers Company Blast Furnace Gas Underfiring	J. K. Munster ³¹
Sensible and latent heat <i>in</i>		
Latent heat coal	13,880	13,600
Sensible heat coal	1	1
Latent heat fuel gas	1,038	1,340
Sensible heat fuel gas	1	1
Sensible heat air in	0	0
Total	14,920	14,942
Sensible and latent heat <i>out</i>		
Latent heat coke	9,380	9,620
Sensible heat coke	485	552
Latent heat gas yield	3,305	3,030
Sensible heat gas yield	159	194
Sensible heat water in gas	129	130
Latent heat in tar	777	600
Sensible heat in tar	33	9
Sensible heat in light oils	8
Latent heat in light oils	242	132
Latent heat in ammonia	20	
Sensible heat—lost stack	227	490
Sensible heat radiation and convection	195	179
Total	14,960	14,936
Coke yield	Dry 71.6	74.5
Coal mix	80-20	25.77 percent of volatile matter
Percent water charged	coal 6.5	

figure, namely, leakage of gas into the heating flues or, vice versa, leakage of high-oxygen flue gases into the oven chambers causing combustion. In the American unit heated with blast-furnace gas, this item was carefully watched, and it is believed that heating flue and oven chamber pressures were so closely regulated that little if any such leakage took place. There might possibly be a discrepancy in the weights of the coal. One percent error in weight of the

coal could account for the difference between Davis' and Terres' studies and those cited above. However, the close check between the German and American results would seem to preclude this item.

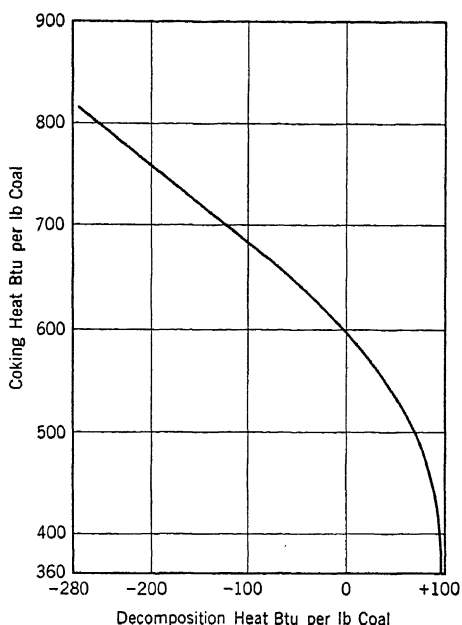
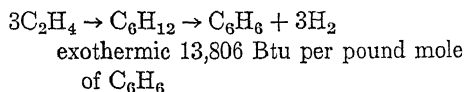
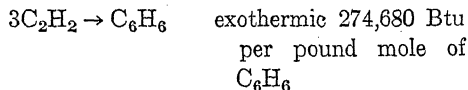


FIG. 37. Relationship between exothermic or endothermic heat of coking (decomposition heat) and heat required for coking (heat required for underfiring minus stack radiation and convection losses). After Terres.³¹

Probably the most plausible explanation that can be given for the large difference between laboratory results based on work of men such as Terres and Davis and actual plant test results lies in the exothermic heat of cracking. Unfortunately the laboratory workers have not studied this phase of the work. The gas obtained from laboratory work should be analyzed and compared with actual coke-oven gas obtained in practice. Should coal when heated break

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up into C_2H_2 , C_2H_4 , H_2 , etc., the following reactions are exothermic:



Dehydrogenating reactions are exothermic. The large amount of hydrogen present in coke-oven gas indicates strongly that the reactions that have taken place are exothermic owing to dehydrogenation.

In any event, the German plant test engineers such as Baum seem to prefer to define efficiency as the ratio of sensible heat in the product of distillation to the actual heat input. If the exothermic heat is low and within the range of experimental error in determining the heat input, then such a definition is correct; otherwise it is wrong.

In one sense such figures show excellent efficiency, but they do not bring out in a pointed way possible savings in underfiring. This can be done only by considering the four points developed in the earlier part of this discussion. These factors in turn must be considered in the light of the product desired. It might be much more desirable to push hotter coke at the expense of underfiring and thus secure a better grade of coke. This factor is a problem for the individual operator. The designer can control the waste-heat temperature by proper design of regenerator checkers.

In order to get perfect heat transfer, the weight of up- and downflow gases multiplied by their respective heats and temperature changes must be equal. This is approximately so for lean gases such as coke producer gas and blast-furnace gas; it is not so for designs of ovens underfired with coke-oven or other "rich" gases. In such

cases, the weight of the upflowing air is much less than that of the downflowing waste gases, which is the sum of the inflow air and inflow fuel gas. Consequently the regenerators are usually designed for pre-heating air and lean gas, and the difference in regenerator efficiency is accepted when burning coke-oven gas.

There must be sufficient regenerator checkers to reduce the temperature of the stack gases to that minimum necessary to carry the waste gases and unfiltered air out of the stack. Excessive checkering costs money, and to attain an unusually low waste-gas temperature may cost so much as to offset any saving in heating gas. Probably the best field open to development lies in radiation and convection losses. Too little consideration has been given to the insulation of the outside of the batteries. Much consideration has been given to appearance. Nearly all batteries of late design are sheathed almost in their entirety with cast and sheet iron with little or no real insulation behind the metal. Some batteries are finished wherever possible with artistic brick with no regard to radiation and convection losses. A thorough study of losses as applied to these matters would yield large dividends.

The following tabulation shows the present trend:

	BLAST-FURNACE		
	GAS: MODERN DESIGN percent	OVEN GAS: OLD KOPPERS percent	OVEN GAS: GERMAN ³³ percent
Stack loss	21.7	36.5	19.67
Radiation and convection	18.7	13.0	11.4
Total loss of fuel gas input	40.4	49.5	31.07

The above figures for stack gases are correct as nearly as can be determined. The

³³ Brückner, H., *Handbuch der Gasindustrie*, R. Oldenbourg, Munich, 1937, 175 pp.

high figure in the second column is due to the large amount of excess air in the waste gas (oxygen content 7.2). The figures for loss by radiant heat and convection are interesting. The modern oven was equipped with steel regenerator fronts, cast-iron jamb brick, and cast-iron door frames. In the other two ovens cited, all these items were made of firebrick. The emissivity of rough cast iron is almost the same as that of brick. A comparison of radiation and convection losses from a German plant and a modern blast-furnace-heated job is given in Table VIII. The skin temperatures of the

TABLE VIII

COMPARISON OF RADIATION AND CONVECTION LOSSES

	German Oven Coke-Oven- Gas Fired		Modern Blast-Furnace- Fired Oven	
	Temper- ature		Temper- ature	
	°F	Btu	°F	Btu
1. Door and frame	332	30	300	68
2. Charging lid and frame	632	18	720	22
3. Clay top	160	12.7	190	22
4. Flue covers	200	10.6	210	12
5. Top buckstays	174	4.5	200	22
6. Small steel	156	0.6	250	4.3
7. Regenerator fireclay in- sulation	178	4	180	19
8. Lower buckstays	115	0.5		
9. Regenerator soles	152	11.5		
Total Btu per pound of coal		92.4		169.3

two examples are not unreasonably far apart. The great difference lies in all probability in methods of figuring convection losses, the Germans usually assuming still air conditions, whereas American engineers commonly measure actual wind velocities and figure accordingly. The large variation in the amount of heat carried away by convection is shown by Heilman³⁴ in some of his papers (see Fig. 38).

³⁴ Heilman, R. H., *Trans. Am. Soc. Mech. Engrs.*, **51**, 287-302 (1929); *Trans. Am. Inst. Chem. Engrs.*, **31**, No. 1, 165-91 (1935).

Another factor not to be overlooked is that all modern batteries are equipped with self-sealing doors, which seat on cast-iron frames that cover the entire brickwork between adjoining ovens. The frames con-

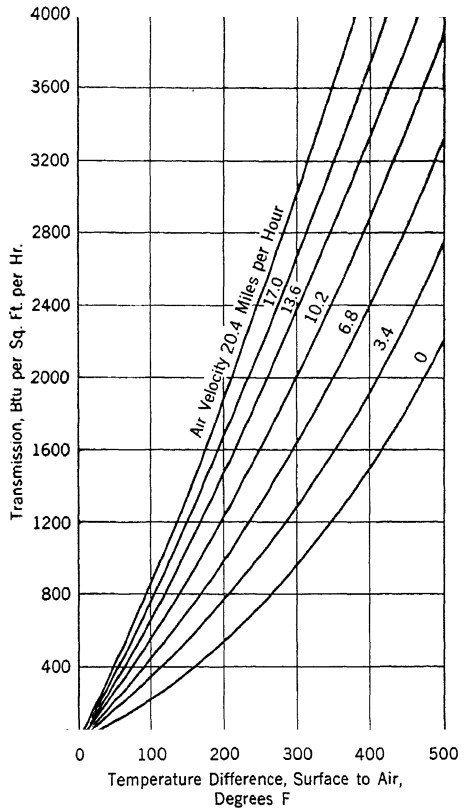


FIG. 38. Heat convected from outer surfaces of coke ovens.³⁴

duct heat from the oven and oven brickwork to the outside. Little can be done about this loss; it is the price to be paid for an important labor-saving item.

The present design of self-sealing door frames completely covers the jamb brick in cast iron, largely for the purpose of securing structural strength of the castings and tying them together. The simplest form of

construction behind the end flue is to carry the silica brickwork to the outside face. This results in a construction as shown in Fig. 39 with 10 inches of silica between the inside of the flue and the outside face. Compare this with the older construction where there is a $4\frac{3}{8}$ -inch layer of silica and inches of clay. Clay is a much poorer

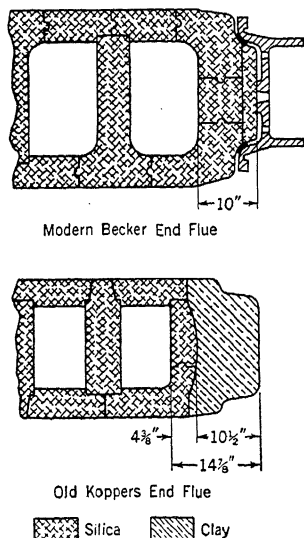


FIG. 39. End flue construction.

conductor of heat, and there is no conducting cast iron. It is difficult to use clay brick between the silica and cast-iron frame on account of the difference in expansion between silica and clay and the difficulty in patching and filling the open joints in the clay. The heat loss at the jambs has been decreased in late designs by having a greater depth of silica and redesigning the cast-iron frame.

The above study indicates in what direction improvements in underfiring can take place. Any improvement in heat economy must be justified on economic grounds; that is, the guiding rule in making improvements in heat economy must be that, if it costs

additional money to save heat, this money must be returned in savings.

METHOD OF HEAT TRANSFER

That almost all the heat is transmitted from flame to flue wall by radiation was nicely shown by van Ackeren³⁵ (see Fig. 40). His work showed 96.4 percent absorbed from the upstream or burning gases in burning coke-oven gas. W. O. Keeling of the Koppers Company has prepared Fig. 41, which shows the amount of heat radiated in burning gases of various calorific values in a standard coke-oven flue.

The main question is distribution of this heat. Lengthwise adjustment has been accomplished very well. The vertical distribution of heat has been difficult, especially with the advent of the higher ovens. When

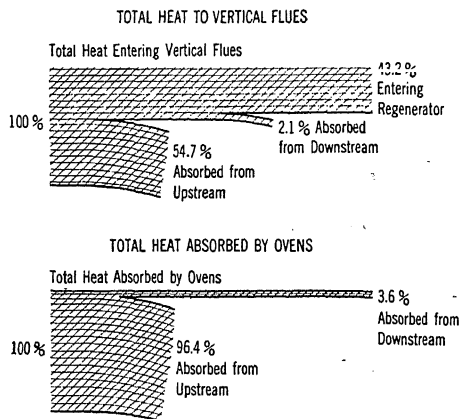


FIG. 40. Heat utilization within coke-oven flues.³⁵

the height of ovens was first raised it was found difficult to heat the tops without over-coking the bottoms and securing "hot bottoms." The first correction in the vertical flued ovens was to raise the location of

³⁵ Van Ackeren, J., *Heat Distribution in Improved Type Koppers Company's Combination Coke and Gas Oven*, Koppers Co., Pittsburgh, 1922, p. 13.

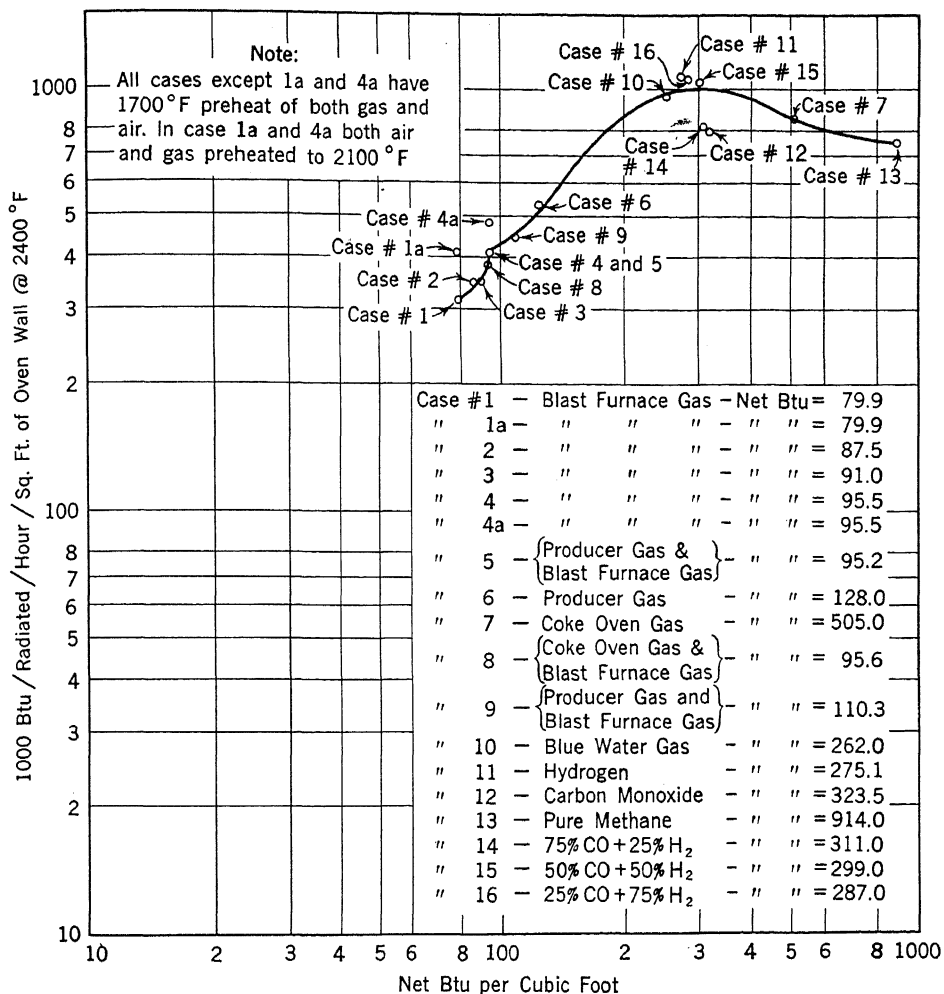


FIG. 41. Effect of net heating value of underfiring gas on relative rates of radiation to coke-oven walls from flames of various fuel gases burned with theoretical volumes of air. Black-body conditions are assumed. Note the break in the curve at approximately 95 Btu.

the horizontal flue and sometimes to decrease the thickness of the oven-wall liners in the upper portion of the oven. Both expedients helped to some extent, but something better was required. In this connection let it be noted that some American and many European builders build oven walls of uniform thickness from top to bot-

tom. Few American and European builders still use graduated thickness of liners. No oven should be built without at least the two bottom rows of liners 1 inch thicker than the next-sized liners above. Lower liners are slowly gouged out by the action of the pusher shoe grinding coke against the wall. Sometimes pieces of metal, bolts,

etc., can become wedged between the masonry and the shoe, causing gouging. Long experience shows that the lower brickwork must have additional protection.

With the advent of producer-gas and subsequently blast-furnace-gas heating, improved vertical heating was observed. The difference was so marked and the heating so nearly perfect³⁶ that considerable thought was devoted to the cause of this better heating. The outstanding fact in burning producer or blast-furnace gas is the relatively high proportion of carbon monoxide with respect to hydrogen and the nonluminosity of the flame. The rate of flame propagation burning carbon monoxide is much slower than when hydrogen is burned. This fact, coupled with the greater amount of inerts (nitrogen and carbon dioxide) in the burning gases, caused a longer flame. Koppers³⁷ in 1916 proposed to pump stack gases into the inflowing air at the base of the regenerator. Though this scheme gave greatly improved results in burning oven gas it was costly to install and operate, and consequently the idea remained only a technical curiosity until 1929, when Kelting³⁸ patented a method of passing waste gas from the bottom of a downflow flue into the bottom of an upflow flue by leaving an opening of proper dimension between the two flues, at the bottoms of the pair of flues. Patents of Tot-

³⁶ The question may be raised: what is perfect heating? It is a difficult one to answer, and every operator has his own views. However, in general, perfect heating means that the temperature of the resultant coke should be constant within 50° F in a vertical line from top to bottom, excluding the top foot and bottom foot and excluding the area covered by horizontal flue. "Perfect heating" will not take care of temperature inequalities caused by packing of coal due to method of charging, segregation due to size of coal, etc.

³⁷ Koppers, H., U. S. Pats. 1,176,066-7 (1916).

³⁸ Kelting, M., U. S. Pat. 1,726,494 (1929).

zek³⁹ showed how this principle could be applied to cross regenerative ovens, and many of these "Kreisstrom" ovens have been built and successfully operated in Europe.

The various builders have tried to improve vertical heating in ways other than recirculating waste gas. Among them may be listed:

1. The introduction of rich fuel gas into the burning flue in stepwise fashion, or from top and bottom, etc.

2. The introduction of rich fuel gas from the bottom and adding air at various levels, limiting combustion in each zone.

3. The use of high and low burners. This method is supposed to correct bottom overheating by introducing rich fuel gas at two different levels in alternating flues. It is being applied in particular to systems with thin bottom liners. (See previous warning.) It has not shown any particular merit in the two-divided oven but is fairly satisfactory in the hairpin oven.

4. The regulation of velocities of air and gas issuing from air and gas nozzles where both are located at the bottom of the flue and at substantially the same level. The method gives good results at the particular coking rate for which these velocities have been determined and the areas of air ports and nozzles designed. Of course, with slower coking times the results are not so satisfactory, although they are still better than were obtained by former practices. The limiting factor in this manner of adjustment is that the air ports must usually be designed to handle lean gas (blast-furnace or producer gas) and air, which sets a limit on what can be done with air port velocities.

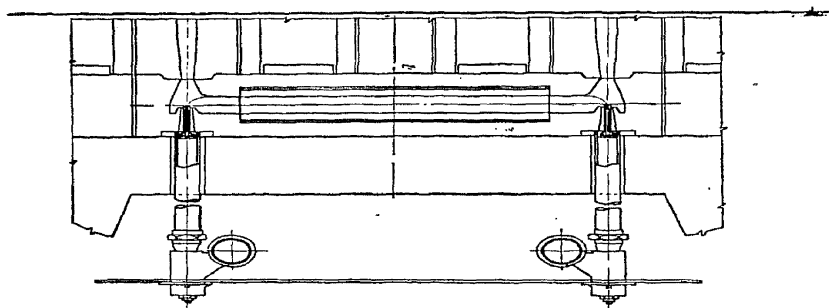
5. A novel scheme for effecting flame attenuation by recirculating combustion prod-

³⁹ Totzek, F., U. S. Pats. 1,957,425 (1934), 1,986,903 (1935).

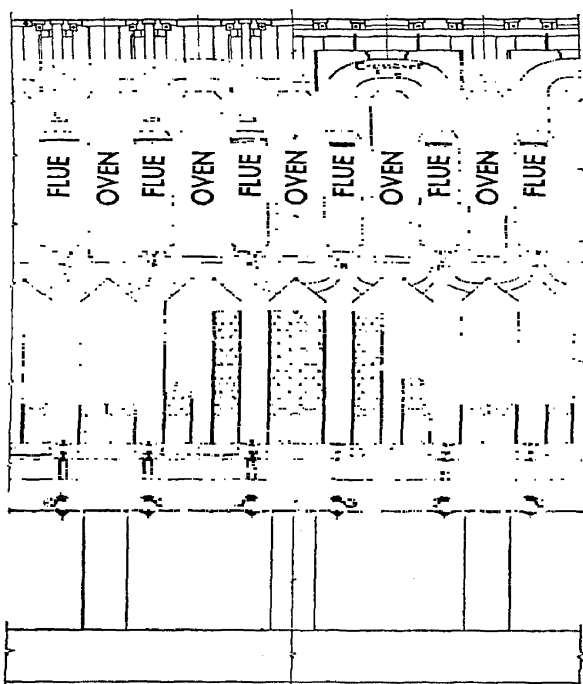
ucts has been developed by van Ackeren of the Koppers Company (see Fig. 42 *a* and *b*). By means of a jet of inflowing rich fuel gas to a battery, van Ackeren withdraws combustion products from a heating flue or flues and provides for the admixing of the jetted rich gas and the withdrawn combustion products before they enter the gas ports of a flame flue. In this way, within the battery itself, the calorific value of a heating gas can be reduced before the gas enters

the flame flues. By certain structural innovations, the basic idea is susceptible of use in either an underjet coke-oven battery or in one designed to distribute heating gas by means of the well-known "gas-gun." If rich fuel gas is employed as the source of coking heat, improved uniformity is obtained in the vertical heats when this ingenious scheme of recirculation of combustion products is employed, and the quality of coke throughout the oven is improved.

INDUSTRIAL COAL CARBONIZATION



Longitudinal Section through
a Waste-gas Recirculating Duct



Longitudinal Section through the
Inspection Holes and Waste-gas
Recirculating Ducts

Longitudinal Section through
the Crossover Flues and
Air Ports

FIG. 42a. Koppers recirculation coke oven.

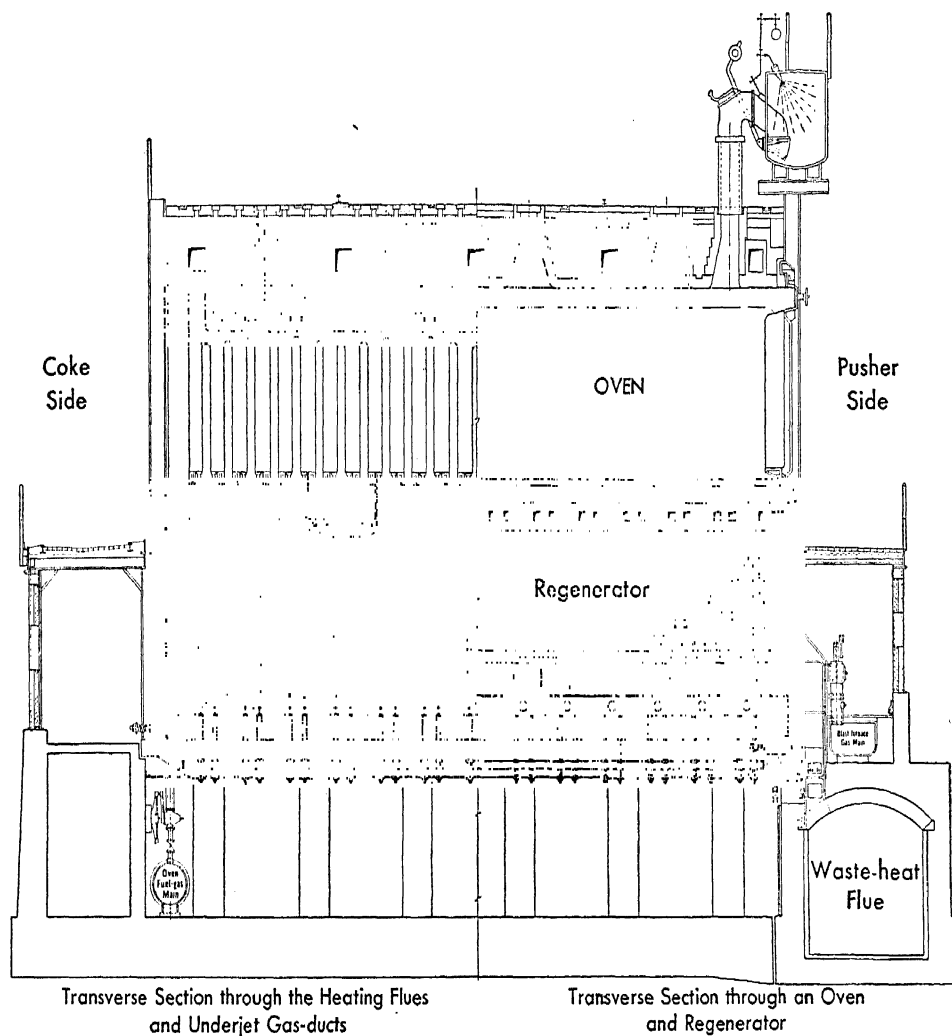


FIG. 42b. Koppers recirculation coke oven.

CHAPTER 22

DEPENDENCE OF YIELDS OF PRODUCTS ON TEMPERATURE AND RATE OF HEATING *

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In the industrial carbonization of coal, there is competition between rate of distillation and thermal decomposition after the distillation products are evolved from the plastic layer, owing to exposure to the higher temperatures of the surfaces over which the products must pass to escape from the retort or oven. The average time of exposure for a given flue temperature is determined largely by the width and height of the oven or retort, and the maximum temperature of exposure varies with the flue temperature. Rate of heating depends on both flue temperature and width of oven; accordingly, when the flue (or carbonizing) temperature is changed, the rate of heating will change and experimental determination of the separate effects of these variables on the yields of carbonization products is difficult, if not impossible. At first it would appear that by making suitable combinations of carbonizing temperature and width of oven the effect of these factors on yields of products might be determined separately. For example, the same width of oven or retort can be used for different carbonizing temperatures and different widths of oven for the same car-

bonizing temperatures. This procedure has been followed in the Bureau of Mines Laboratory, as will be shown later, but it is not believed practical in industrial-scale apparatus because constant wall temperatures are not maintained.

Undoubtedly batteries of ovens have been operated on the same coals at different flue temperatures, because it often has been necessary to reduce the throughput during times of decreased demand for coke, and lowering the flue temperatures is a practical means of doing so. However, when the flue temperatures are changed, the relationship of heat stored in the refractories to that transferred to the charge also is changed, so that the effective inner-wall temperature probably does not change in proportion to the changes in flue temperatures. Varying the flue temperatures would give the overall effect as referred to the flue temperatures in a given type of oven, but without knowledge of effective inner-wall temperatures the flue temperatures probably would not be generally significant. Rummel¹ has shown the general relationship between heat stored and heat

* Published by permission of the Director, Bureau of Mines, United States Department of the Interior.

¹ Rummel, K., *Trans. Fuel Conf., World Power Conf., London*, **2**, 27-68 (1928). See also Steinschläger, M., *Arch. Eisenhüttenw.*, **3**, 331-8 (1929).

transferred in a coke oven, and Baum² has shown the effect on the inner-wall temperature of varying the flue temperature and consequently the carbonizing time; however, Baum's experiments were applied to ovens differing somewhat in width (450 and 400 millimeters), and he did not give the effect on yields of carbonization products.

It is common industrial practice to employ ovens of different widths, and approximately the same flue temperatures have been used in such ovens, but no strictly comparable data have been published showing the effect of width of oven on the yields of products.

DEPENDENCE OF CARBONIZING TIME ON WIDTH OF OVEN

Mott and Wheeler³ have stated that "the coking time is directly proportional to the square of the width of the oven." They assumed a coking time of 36 hours for a 21-inch oven having clay refractories with the flues maintained at 1,100° C and stated that "the following coking times should apply to other widths of ovens:

"Width of oven, inches	20	18	16	14
"Coking time, hours	32.5	26.5	21	16"

Their figures for silica ovens at a flue temperature of 1,400° C were:

Width of oven, inches	21	20	18	16	14
Coking time, hours	24	22	17.5	14	11

These figures agree closely with those calculated from the formula for flat ovens derived by Burke, Schumann, and Parry⁴ partly by experiment and partly by deduc-

tions from the theory of heat conductivity. Their formula for a flat retort is:

$$\text{Coking time} = 2FR^2$$

where $2R$ is the width of the oven and F is a factor depending on the wall temperature. Mott and Wheeler stated further:

The rate of heating is naturally related to the coking time. The most important period is during the plasticity of the coal, over the temperature range 400 to 500° C. Taking the wider range of temperature 300 to 600° C so as to include this important period, the average rate of rise of temperature in a 20-inch oven coking in, say, 30 hours is 1.0° C per minute at $\frac{1}{4}$ width, whilst in a 14-inch oven coking in 11 hours the average rate of rise of temperature at $\frac{1}{4}$ width will be 2.5° C. Such variations in the rate of heating are not great, in comparison with rates of heating obtainable in laboratory tests, but they have important effects.

It must be remembered that Mott and Wheeler were thinking primarily of the effect on the *quality of the coke*, as this was the subject under discussion.

One difficulty in obtaining comparable results on yields of products from industrial carbonization practice where several widths of ovens are used lies in the fact that different coals, or blends of coals, are used at different plants; furthermore, operating conditions are likely not to be comparable, and recovery practice varies, particularly in plants of different designs. For these reasons, data on the effect of rate of heating and carbonizing temperature obtained in the small-scale testing equipment used by the Bureau of Mines⁵ will be presented later. The method involved keeping the inner-wall temperatures of the retorts constant during the entire carbonizing period at the several temperatures chosen, thus eliminating the factor of storage and release

² Baum, K., *Glückauf*, **65**, 765-76, 812-21, 850-7 (1929).

³ Mott, R. A., and Wheeler, R. V., *The Quality of Coke*, Chapman and Hall, London, 1939, 464 pp.

⁴ Burke, S. P., Schumann, T. E. W., and Parry, V. F., *Proc. Am. Gas Assoc.*, **1930**, 820-55.

⁵ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph 5* (1934), 164 pp.

of heat at the walls which is characteristic of a coke oven. Retorts of different sizes were used at the same carbonizing temperatures, and the overall effect of carbonizing temperature was determined; however, there remained the uncertainty of variation of effective contact of gases and vapors with the heated charges and the possibility that the variation might not be directly proportional to the overall carbonizing time. The process of heat transfer therefore is not purely that of conduction, as Burke, Schumann, and Parry concluded. According to these investigators the carbonizing time for cylindrical retorts is $T = FR^2$, whereas Lowry and his associates⁶ found the relationship $T = FR^{1.54 \pm 0.12}$ by calculation based on a large amount of experimental data. The writer has obtained results in virtual agreement with those of Lowry and believes that the law of squares does not hold strictly and that therefore the process is not one of conduction alone.

DETERMINATION OF RATE OF HEATING IN COKE OVENS

Ryan⁷ considered the rate of travel of the zone of fusion in coke ovens to be a measure of the rate of heating. He observed that the temperature gradient across the zone of fusion is very steep and that gas pressures in this zone are higher than elsewhere in the charge. These facts furnished the basis of two methods whereby he could follow the progress of the plastic zone: the temperature-drop and the gas-pressure methods. In applying the former he observed temperatures at uniform points across the charge and plotted isochronic temperature curves from the walls to the

center of the oven. From these curves he could determine the points of steepest temperature gradients and so find and follow the progress of the fusion zone. He also applied the pressure-drop method, originally developed by Wilson.⁸ In this method $\frac{1}{4}$ -inch open pipes were introduced at intervals across the charge. The pipes were connected outside the oven to manometers by which the times of maximum pressure could be observed and the progress of the fusion zone followed.

It should be noted that the temperature limits for the plastic range (575 to 750° F) given by Ryan are much too low. The figures 400 to 500° C (752 to 932° F) given by Mott and Wheeler⁹ are about right. Some lower-rank coking coals begin to fuse at temperatures around 390° C, but most of them begin to fuse at 400° C or a few degrees higher. The range in temperature at which fusion begins for different coking coals is remarkably small, and the precision with which fusion can be observed by several test methods is worthy of note.⁹

With the plastic range fixed at about 400 to 500° C, it is possible to approximate closely the rate of progress of the plastic zone from earlier work,¹⁰ in which temperature measurements were made at fixed intervals across the coking charge and for which time-temperature curves have been published. The trend of such curves is characteristic of the layer-coking process, regardless of whether the retort or oven is round or rectangular, as is clear upon comparison of Fig. 1, taken from Simmersbach and applying to a coke oven, with Fig. 2, using a cylindrical retort.⁵

⁸ Wilson, D. W., *ibid.*, 1923, 952-64.

⁹ Brewer, R. E., and Triff, J. E., *Ind. Eng. Chem., Anal. Ed.*, 11, 242-7 (1939).

¹⁰ Simmersbach, O., and Schneider, G., *Grundlagen der Koks-Chemie*, J. Springer, Berlin, 1930, 366 pp.

⁶ Lowry, H. H., Landau, H. G., and Naugle, Leah L., *Am. Inst. Mining Met. Engrs., Tech. Publ.* 1332 (1941), 30 pp.

⁷ Ryan, W. P., *Proc. Am. Gas Assoc.*, 1925, 861-78.

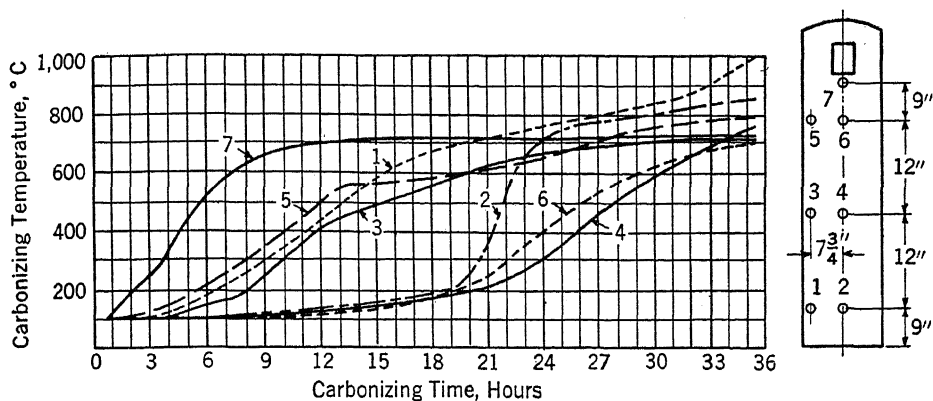


FIG. 1. Carbonizing temperature record—20-inch rectangular coke oven, using dry coal.¹

To measure temperatures at fixed points in a coking charge, thermocouples of appreciable length must be employed, and these must be encased in protecting tubes. If metal tubes are used they are likely to bend and be forced aside by shifting of the charge while it is coking; furthermore, unless the tubes can be maintained parallel to the plastic zone they are likely to conduct heat away from or toward the plastic zone, when the zone is at the point where measurement is being made, and so give a false indication of the temperature. It will be recalled that the temperature gradient

within the zone is steep compared with that elsewhere in the charge. If refractory tubes are used, they are likely to break. The shifting of the charge during coking may affect the accuracy of pressure measurements when the pressure method is used; furthermore, plastic coal may enter the ends of the tubes and coke there, giving pressures entirely too high and not necessarily coincident with the passage of the plastic zone in the oven. These difficulties have been encountered in the Bureau of Mines laboratories when temperature and pressure were measured during coking tests.

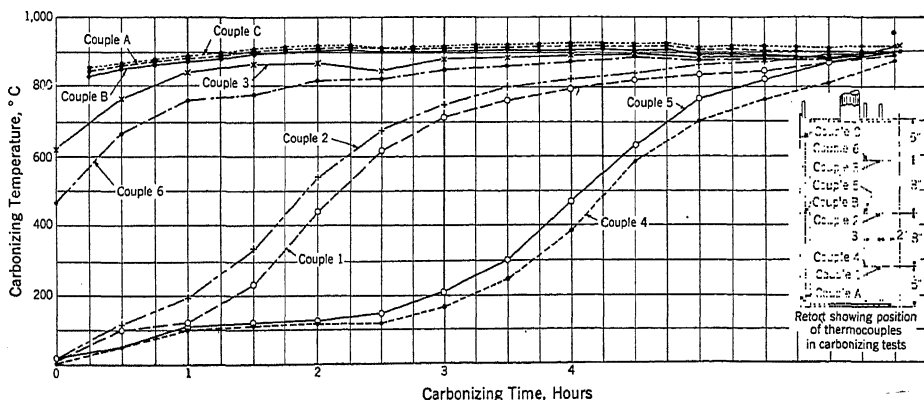


FIG. 2. Carbonizing temperature record—13-inch BM-AGA retort heated in an electric furnace.⁵

IMPORTANCE OF THE PLASTIC STAGE IN CARBONIZATION IN DETERMINING YIELDS OF CARBONIZATION PRODUCTS

Mott and Wheeler³ have stated that "the most important period is during the plasticity of the coal, over the temperature range 400 to 500° C." This statement applies particularly to the influence on the quality of the coke. In the plastic period of the coking process, the most important chemical and physical changes evidently take place, because the so-called primary decomposition of the coal substance occurs during this period. It has been observed that the temperature range from the point of fusion to the point at which the coal sets to form coke is fixed within narrow limits for all coals; therefore it can be inferred that exposure to temperatures within the plastic range does not vary the yields of products in industrial coking provided that the thickness of the plastic layer is constant. If the time of passage through the plastic zone, or the rate of heating, is varied it should be possible to vary the yields of products, because by so doing the time of exposure to the plastic range of temperatures can be varied.

It is possible that the thickness of the plastic layer differs for different coking coals, and if so some variation in yields of carbonization products from this cause would be expected. Sapozhnikov¹¹ found the thickness to vary from approximately 15 to 35 millimeters. However, the writer has not been able to verify Sapozhnikov's results. (See also pp. 280-98.)

Juettner and Howard¹² worked with a

¹¹ Sapozhnikov, L. M., and Bazilevich, L. P., *Investigation of the Coking Process: Classification of Coals and Calculation of Coking Mixtures on the Basis of the Plastometric Method*, State Scientific Publishing House of Ukraine, Kharkov, 1935, pp. 34-54.

¹² Juettner, B., and Howard, H. C., *Ind. Eng. Chem.*, **26**, 1115-8 (1934).

molecular still at extremely low pressures and at maximum temperatures only slightly above the upper limit of the plastic range. The products from a thin layer of coal were chilled by a liquid-air condenser placed within the mean free molecular path, so that the products, once formed, suffered minimum thermal decomposition. They investigated rate of heating and found that rapid heating resulted in larger yields of condensate than exhaustive heating stepwise to the same maximum temperatures. Admittedly their experimental conditions were extreme; however, the results prove that rate of heating through the plastic range is important. These investigators also brought out the interesting fact that larger yields of condensate were obtained by heating at atmospheric pressure to 400° C than by heating in a vacuum to that temperature. Evidently other factors besides rate of heating and maximum temperature affect yields of products within this temperature range—probably the solvent effect of tars remaining for an appreciable length of time in contact with the charge, as the writers suggested.

In the Bureau of Mines Survey of Carbonizing Properties of American Coals,¹³ the Fischer assay¹⁴ with 50 grams of coal and the BM-AGA retort with 80 to 90 pounds have been used to determine the yields of carbonization products at 500° C. The carbonizing time in the BM-AGA retort was 30 to 35 hours compared to 2.5 hours in the Fischer retort, or more than 10 times as long. As a matter of fact, virtually all the tar was obtained from the Fischer retort during the first hour. The comparison in yields of carbonization products from the two retorts for Pond Creek

¹³ Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **344** (1931), 107 pp.

¹⁴ Fischer, F., and Schrader, H., *Ges. Abhandl. Kenntnis Kohle*, **5**, 55-64 (1920).

high-volatile A coal¹⁵ shown in Table I illustrates the differences which may be due to carbonizing time.

yield of coke was about 1.9 percent and that of gas about 4 percent less at the higher rate of heating.

TABLE I

COMPARISON OF YIELDS OF PRODUCTS OBTAINED ON CARBONIZING A HIGH-VOLATILE A COAL TO 500° C AT DIFFERENT RATES¹⁵

Retort	Maximum Temperature °C	Carbonizing Time hours	Yields of Products				Yields per Ton of Coal	
			Coke	Gas	Tar	Liquor	Gas cubic feet	Tar gallons
			percent of coal charged					
Fischer	500	2.5	76.7	4.9	12.0	5.5	1,950	28.9
BM-AGA	500	30.5	77.8	5.7	9.1	6.3	2,550	21.6

This coal ceased to be plastic at 491° C, so that the maximum carbonization temperature may be looked upon as the upper limit of the plastic range within the limits of experimental error. The main effect on yields of products of extending the carbonization time more than tenfold appears to be decomposition of about 24 percent of the tar into gas, coke, and liquor.

EFFECT OF RATE OF HEATING THROUGH THE PREPLASTIC RANGE ON YIELDS OF CARBONIZATION PRODUCTS

Warren¹⁶ has studied the effect on yields of carbonization products of changing the rate of heating through the preplastic range. He heated 110 grams of 20- to 80-mesh coal in a 1-inch 18-8 alloy steel tube at rates of 1.4 and 21.8° C per minute through the preplastic range, the most rapid rate thus being more than 15 times the slowest. This difference in heating through the preplastic range—25 to 390° C—changed the yield of condensable liquids by more than 13 percent, the higher yield corresponding to the more rapid rate; the

The results show that during the slow heating through the preplastic range in a coke oven, where the maximum variation is only a few degrees per minute, physical or chemical changes, or both, may take place that modify the so-called primary decomposition of the coal. However, the variation attainable in heating through the preplastic range in present coke-oven practice is so small that it will be impracticable to take advantage of this knowledge by varying the operation. The coal could, of course, be preheated rapidly, as in a rotary retort, then charged hot into the ovens. During 1928, the writer had the good fortune to observe some tests that the late Professor Parr¹⁷ was making at Urbana, Ill., in which he preheated the coal in a rotary retort just short of the fusion temperature and then charged it hot into a 2-ton Russell slot-type oven. He was able to reduce the carbonizing time about half. This advantage would seem important, but as far as the writer knows no industrial developments have resulted from the research. (See also pp. 848-59.)

Undoubtedly changes (other than elimination of water, carbon dioxide, etc.) take place in the coal substance at temperatures below that at which the coal fuses. King

¹⁵ Fieldner, A. C., Davis, J. D., Selvig, W. A., Reynolds, D. A., Sprunk, G. C., and Auvil, H. S., *U. S. Bur. Mines, Tech. Paper* 596 (1939), 46 pp.

¹⁶ Warren, W. B., *Ind. Eng. Chem.*, **27**, 1350-4 (1935).

¹⁷ Parr, S. W., unpublished work.

and Willgress¹⁸ distilled small quantities of oils from coking coal at 215° C. Thiessen and Sprunk¹⁹ studied the effect of preheating coal at temperatures below its fusion point on the petrographic structure. They detected fusion of cuticles and resins and slight exudation of oils. At the fusion temperature the coal became opaque, and changes in structure could no longer be observed by the method used, which consisted of making thin sections of the material and following changes in structure under the microscope by transmitted light. Work in the Bureau of Mines laboratories has shown²⁰ that the fluidity of a coal in the plastic range can be reduced and its fusion temperature raised by prolonged heating in the preplastic range. The lowering of the fluidity is considerable; it may be caused by the predominance of large molecules formed in rendering the coal compounds less sensitive to temperature by preheating, as Warren¹⁶ has suggested.

WORK OF BUREAU OF MINES BEARING ON
EFFECT OF CARBONIZING TEMPERATURE AND
RATE OF HEATING ON YIELDS OF CARBONIZ-
ATION PRODUCTS

CARBONIZING TEMPERATURE

In the Survey of Carbonizing Properties of American Coals being conducted by the Bureau of Mines each coal is tested in a retort 13 inches in diameter (80- to 85-pound charges) at 500, 600, 700, 800, and 900° C, and also in a retort 18 inches in diameter (180- to 190-pound charges) at 800, 900, and 1,000° C, and the yields and quality of carbonization products are determined. More than 60 coking coals have

been tested; for 30 or more of these, the size of the retorts and temperatures were as stated. The retorts are charged cold into the furnace, which has been heated to a temperature somewhat above that desired, so that soon after charging the retort wall attains the test temperature at which it is kept constant automatically during the entire carbonizing period. Figure 3 for Upper Banner Seam coal²¹ illustrates the dependence of yields of products on carbonizing temperature. Except for minor differences, this coal shows trends that are characteristic of all coals tested.

The yield of gas (volume basis) is almost a straight-line function of the carbonizing temperature over this range of temperature. Figure 4 shows that the yield on the basis of Btu in gas per pound of coal is similarly related to the carbonization temperature; however, the curve tends to flatten at the higher temperatures, indicating that raising the temperature much beyond 1,000° C would not increase the yields.

The yield of tar approaches inverse proportionality to carbonizing temperature; however, in Fig. 3 the yield at 500° C is slightly less than that at 600° C. This result is characteristic of high-rank coals, but with coals of lower than high-volatile A rank the yield at 500° C usually is higher than that at 600° C. In the carbonization process there is competition between distillation and decomposition, and evidently with this high-rank coal the longer time of contact at 500° than at 600° C gave decomposition the advantage. Coals of different rank behave somewhat differently in this regard.

The yield of coke decreased as the temperature was raised to 800° C and then ap-

¹⁸ King, J. G., and Willgress, R. E., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper 16* (1927), 19 pp.

¹⁹ Thiessen, R., and Sprunk, G. C., *Fuel*, **13**, 116-25 (1933).

²⁰ Fieldner, A. C., *U. S. Bur. Mines, Information Circ. 6992* (1938), 44 pp.

²¹ Fieldner, A. C., Davis, J. D., Thiessen, R., Selvig, W. A., Reynolds, D. A., Brewer, R. E., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper 554* (1938), 81 pp.

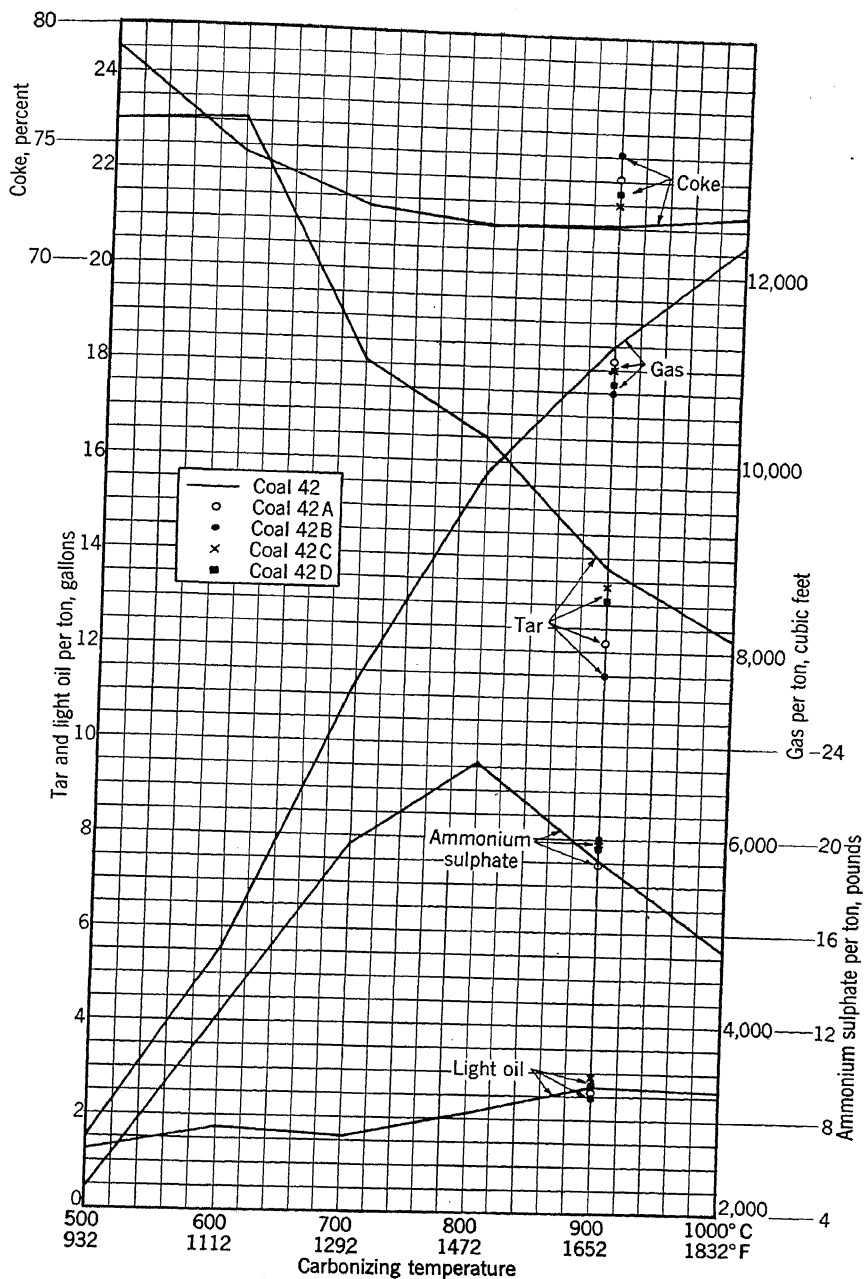


FIG. 3. Yields of carbonization products from Upper Banner Seam coal.²¹

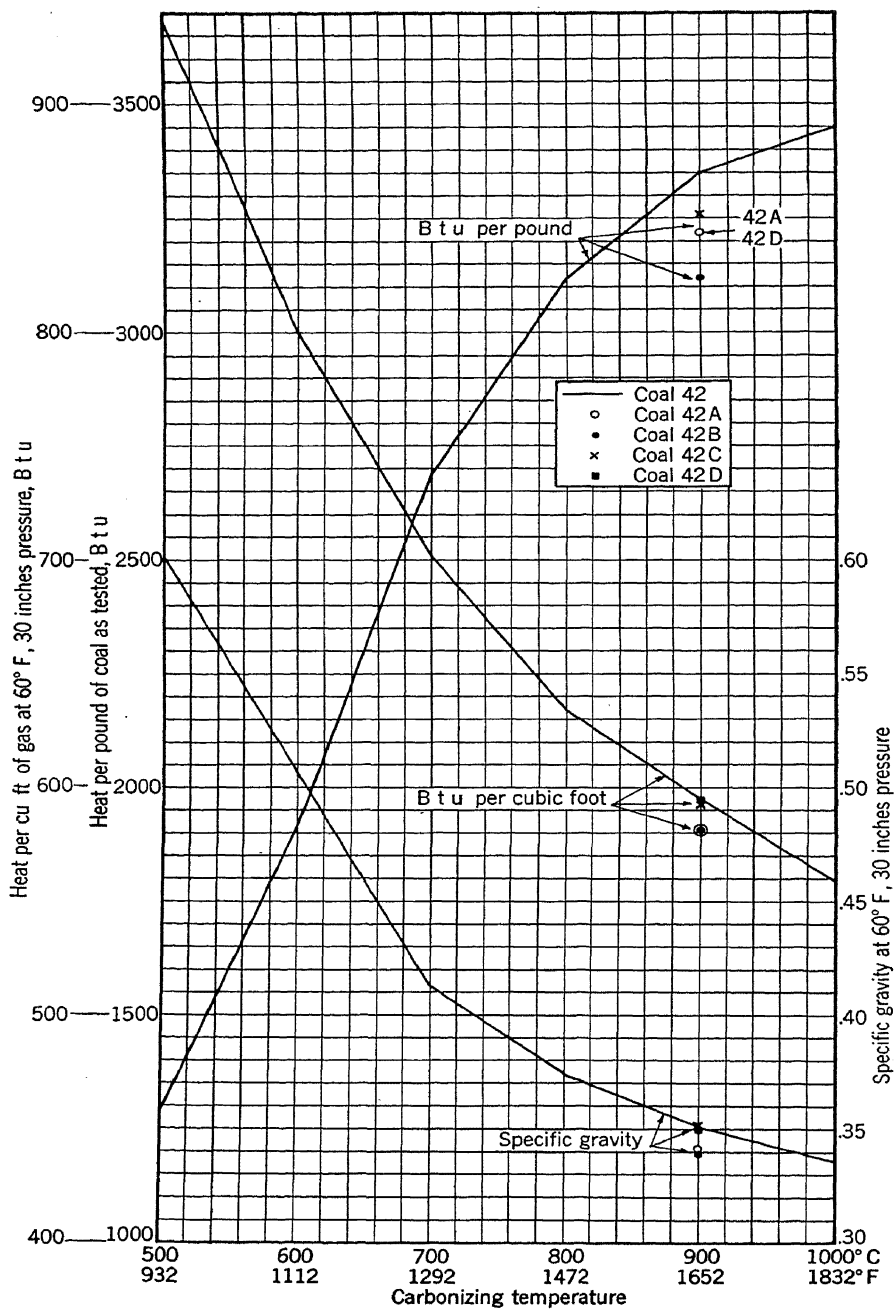


FIG. 4. Physical constants of gas from carbonization of Upper Banner Seam coal.²¹

proached constancy. There was a tendency for slight increase at 1,000° C, probably because of increased graphitization.

The yield of light oil approached a maximum at 900° C and that of ammonium sulfate at 800° C. Contact with the iron walls of the retort probably decomposes ammonia more rapidly than would contact with a refractory wall at higher temperatures. The yields at 900 and 1,000° C were always lower than those obtained in coke ovens. Lunge²² has given detailed results of experiments showing that contact with iron decomposes ammonia more rapidly over the temperature range in question than contact with refractories.

The effect of blending Upper Banner coal with 20 and 30 percent of Beckley and Sewell coals on the yields of products is shown for the 900° C tests. On the "as-received" or as-carbonized basis the volatile-matter content of Upper Banner coal was 31.8 percent, that of Beckley coal was 17.9, and that of Sewell coal was 26.5. The effect of adding the lower-volatile coals to the Upper Banner coal was to increase the yields of coke, mostly at the expense of the tar. The yield of gas was also lowered to some extent.

EFFECT OF RATE OF TRAVEL OF PLASTIC ZONE AND VARIATION IN CARBONIZING TEMPERATURE

In the preceding section the main variable as far as effect is concerned probably is carbonizing temperature; however, as a retort of the same size was used for all temperatures the carbonizing time, or rate of travel of the plastic zone, also differed considerably. The carbonizing time in the 13-inch retort at 500° C was about 30 hours, whereas at 900° C it was about 7 hours.

The time varies somewhat with different coals. Tests at 1,000° C were made in the 18-inch retort only.

For coals tested more recently, data are available on the effect of varying the rate of travel of the plastic zone at the two temperatures 800 and 900° C (in the neighborhood of effective wall temperatures in coke ovens). Table II gives the results for 20 coals; by changing the diameter of the retort the rate of travel of the plastic zone is changed about 14 percent. The effects on yields of products of changing the rate of travel by this amount at both temperatures are small but significant on an average. Except for the light oil and ammonium sulfate, the yields from the two retorts would be considered hardly outside of the limits for duplicate determinations. It is clear that the large retort yields slightly more coke and gas and less tar than the small one. The variations are of the order of 1 percent of the product, or less. The effect of raising the carbonizing temperature from 800 to 900° C, on the other hand, is to increase the yield of gas and light oil by about 10 percent and decrease that of tar by a similar percentage. The yield of coke remains virtually unchanged. The yields of ammonium sulfate are greater at 800° C and in the large retort; the yield at 800° C in the large retort is only slightly less than that normally obtained from a coke oven.

In conclusion, in industrial carbonization of coal it is virtually impossible to separate the effects of rate of heating and carbonizing temperature on the yields of carbonization products, because when one factor changes so does the other. Rate of heating has been defined as the rate of travel of the plastic layer, and this appears logical, because it is within the plastic layer that the most pronounced physical and chemical changes of the coking process take place.

²² Lunge, G., *Coal Tar and Ammonia*, Part III, *Ammonia*, Gurney & Jackson, London, 1916, 1658 pp.

YIELDS OF CARBONIZATION PRODUCTS

TABLE II

COMPARATIVE YIELDS OF CARBONIZATION PRODUCTS, AS-CARBONIZED BASIS, 13-INCH AND 18-INCH RETORTS AT 800 AND 900° C

Retort Diam- eter No. inches	Coal	Bed and Rank	Carbon- izing Temper- ature °C	Yields *				Yields per Ton of Coal *						
				Coke	Gas percent by weight of coal	Tar	Light Oil	Free Ammonia	Liquor	Gas cubic feet	Tar	Light Oil		
												In gallons	In 170°C gallons	In Tar to 170°C (NH ₄) ₂ SO ₄ pounds
41	13	Beckley low-volatile	800	82.6	10.4	2.7	0.48	0.188	3.5	9,350	5.6	1.34	0.15	17.7
41	18	Beckley low-volatile	800	82.6	10.6	2.6	0.53	.190	3.9	9,350	5.4	1.49	0.16	19.7
41	13	Beckley low-volatile	900	82.2	11.0	2.5	0.53	.179	3.6	10,600	5.0	1.47	0.07	16.2
41	18	Beckley low-volatile	900	82.7	11.8	2.3	0.52	.158	3.6	10,750	4.7	1.45	0.12	16.5
43	13	Dorothy high-volatile A	800	70.1	14.4	8.0	1.03	.168	5.7	9,400	16.5	2.87	1.01	22.0
43	18	Dorothy high-volatile A	800	70.4	14.7	7.8	0.97	.179	5.4	9,550	16.2	2.70	1.09	24.0
43	13	Dorothy high-volatile A	900	70.0	15.5	7.1	1.17	.160	5.7	10,950	14.2	3.20	0.58	21.4
43	18	Dorothy high-volatile A	900	70.7	15.8	6.7	1.20	.170	5.3	11,000	13.5	3.30	0.58	20.6
44	13	Powellton A high-volatile A	800	71.5	14.2	7.8	0.96	.225	4.8	9,650	16.2	2.73	0.65	21.9
44	18	Powellton A high-volatile A	800	71.7	14.2	7.7	0.90	.228	4.9	9,750	15.9	2.53	0.76	22.8
44	13	Powellton A high-volatile A	900	71.1	15.2	7.1	1.16	.204	4.7	11,000	14.3	3.17	0.41	19.4
44	18	Powellton A high-volatile A	900	71.4	15.3	6.8	1.16	.202	4.7	11,200	13.8	3.20	0.50	20.0
46	13	Eagle high-volatile A	800	71.8	13.2	7.3	0.92	.186	5.7	9,200	15.2	2.62	0.81	21.9
46	18	Eagle high-volatile A	800	72.4	13.3	6.6	1.07	.194	5.8	9,250	14.0	3.04	0.80	22.6
46	13	Eagle high-volatile A	900	71.6	14.3	6.4	1.12	.225	5.5	10,550	12.8	3.10	0.44	18.8
46	18	Eagle high-volatile A	900	72.1	14.5	6.2	1.07	.168	5.5	10,650	12.5	2.97	0.44	19.2
42	13	Upper Banner high-volatile A	800	71.9	14.2	7.9	0.80	.200	4.3	9,650	16.3	2.25	0.85	21.9
42	18	Upper Banner high-volatile A	800	72.0	13.9	8.0	0.76	.172	4.8	9,850	16.5	2.13	1.17	23.2
42	13	Upper Banner high-volatile A	900	71.7	14.8	7.5	0.88	.167	4.4	11,050	15.0	2.42	0.65	18.7
42	18	Upper Banner high-volatile A	900	72.1	14.9	7.1	0.98	.148	4.5	11,250	13.8	2.70	0.70	19.1
52	13	Pittsburgh high-volatile A	800	68.1	13.7	8.9	0.86	.156	7.1	8,750	18.7	2.44	1.08	22.5
52	18	Pittsburgh high-volatile A	800	68.2	13.6	8.7	0.97	.128	6.9	8,900	18.4	2.74	1.36	19.7
52	13	Pittsburgh high-volatile A	900	68.2	14.9	7.8	1.19	.135	7.0	10,300	16.0	3.27	0.88	18.8
52	18	Pittsburgh high-volatile A	900	68.0	14.5	7.9	1.09	.141	7.0	10,000	16.3	3.01	0.85	18.1
53	13	Pond Creek high-volatile A	800	70.2	13.2	7.6	0.83	.143	6.6	9,150	15.8	2.35	0.90	18.8
53	18	Pond Creek high-volatile A	800	70.5	13.1	7.5	0.90	.138	6.9	9,000	16.1	2.59	1.13	21.0
53	13	Pond Creek high-volatile A	900	70.1	14.0	6.6	0.98	.111	6.6	10,300	13.6	2.70	0.77	16.2
53	18	Pond Creek high-volatile A	900	70.3	14.4	6.3	1.01	.126	6.7	10,350	13.1	2.80	0.58	17.3
47	13	Lower Kittanning (unwashed) low-volatile	800	83.9	10.4	1.9	0.41	.194	3.2	9,050	3.9	1.11	0.09	18.0
47	18	Lower Kittanning (unwashed) low-volatile	800	83.9	10.6	1.7	0.43	.185	3.2	9,350	3.4	1.19	0.07	19.1
47	13	Lower Kittanning (unwashed) low-volatile	900	83.6	10.9	1.7	0.45	.149	3.2	10,300	3.6	1.21	0.03	13.9
47	18	Lower Kittanning (unwashed) low-volatile	900	83.6	11.5	1.5	0.45	.144	3.0	10,800	3.1	1.23	0.03	14.4

YIELDS OF CARBONIZATION PRODUCTS

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48	13	Lower Kittanning (washed) low-volatile	800	82.5	10.0	1.6	0.42	0.143	5.1	8,600	3.3	1.15	0.09	16.0
48	18	Lower Kittanning (washed) low-volatile	800	82.3	10.4	1.7	0.42	.156	5.3	9,000	3.6	1.17	0.10	19.2
48	13	Lower Kittanning (washed) low-volatile	900	82.0	11.1	1.6	0.46	.131	4.8	10,250	3.2	1.24	0.04	13.1
48	18	Lower Kittanning (washed) low-volatile	900	82.0	11.1	1.4	0.49	.130	4.8	10,400	2.8	1.33	0.03	15.2
50	13	Upper Kittanning (unwashed) low-volatile	800	82.7	10.3	2.0	0.39	.204	4.1	8,650	4.1	1.07	0.05	19.2
50	18	Upper Kittanning (unwashed) low-volatile	800	82.7	10.5	1.9	0.44	.194	4.0	8,800	3.8	1.20	0.13	19.0
50	13	Upper Kittanning (unwashed) low-volatile	900	82.3	11.0	1.6	0.48	.184	3.1	10,150	3.2	1.30	0.03	15.7
50	18	Upper Kittanning (unwashed) low-volatile	900	82.3	11.0	1.6	0.51	.160	3.9	10,150	3.3	1.39	0.05	14.9
51	13	Upper Kittanning (washed) low-volatile	800	83.0	10.7	1.9	0.40	.237	3.6	8,900	3.9	1.09	0.10	20.7
51	18	Upper Kittanning (washed) low-volatile	800	82.6	10.8	1.8	0.50	.222	3.4	8,950	3.7	1.39	0.09	19.3
51	13	Upper Kittanning (washed) low-volatile	900	82.7	11.3	1.9	0.50	.196	3.4	10,100	3.7	1.37	0.04	16.7
51	18	Upper Kittanning (washed) low-volatile	900	82.2	11.3	1.6	0.48	.161	3.3	10,400	3.1	1.30	0.04	14.9
55	13	Sewell medium-volatile	800	79.8	11.0	4.2	0.58	.198	3.6	9,250	8.6	1.03	0.22	19.1
55	18	Sewell medium-volatile	800	80.0	11.1	4.0	0.58	.196	3.8	9,350	8.3	1.64	0.32	18.8
55	13	Sewell medium-volatile	900	79.5	11.7	3.8	0.68	.177	3.5	10,600	7.7	1.86	0.11	15.9
55	18	Sewell medium-volatile	900	80.0	11.8	3.4	0.64	.169	3.4	10,650	6.9	1.77	0.14	16.1
56	13	Pocahontas No. 3 low-volatile	800	84.1	10.0	2.2	0.42	.174	3.0	9,100	4.4	1.16	0.09	14.7
56	18	Pocahontas No. 3 low-volatile	800	84.3	10.0	2.2	0.41	.183	2.9	9,050	4.5	1.13	0.12	15.7
56	13	Pocahontas No. 3 low-volatile	900	84.1	10.5	2.1	0.50	.149	2.5	10,300	4.2	1.34	0.04	12.6
56	18	Pocahontas No. 3 low-volatile	900	84.0	10.6	2.0	0.50	.149	2.7	10,450	4.1	1.36	0.08	13.4
57	13	Pocahontas No. 4 low-volatile	800	84.5	10.1	2.1	0.47	.192	3.0	8,850	4.3	1.28	0.16	16.9
57	18	Pocahontas No. 4 low-volatile	800	84.5	10.4	1.9	0.46	.197	2.6	9,000	3.7	1.26	0.09	19.8
57	13	Pocahontas No. 4 low-volatile	900	84.2	10.6	1.6	0.46	.168	1.9	10,400	3.1	1.24	0.09	14.3
57	18	Pocahontas No. 4 low-volatile	900	84.3	10.6	1.6	0.48	.164	2.4	10,250	3.2	1.29	0.06	14.5
58	13	Lower Banner medium-volatile	800	79.3	11.3	3.4	0.66	.174	4.3	8,700	7.0	1.84	0.34	18.5
58	18	Lower Banner medium-volatile	800	79.2	11.4	3.5	0.58	.183	4.7	8,750	7.4	1.64	0.48	21.9
58	13	Lower Banner medium-volatile	900	78.9	11.7	3.3	0.72	.146	4.2	10,000	6.6	1.96	0.15	14.7
58	18	Lower Banner medium-volatile	900	79.2	11.8	3.2	0.70	.140	4.2	10,150	6.4	1.92	0.25	15.2
59	13	Upper Freeport high-volatile A	800	72.6	12.1	7.0	0.61	.161	5.9	8,900	14.2	1.71	0.70	18.0
59	18	Upper Freeport high-volatile A	800	72.4	12.1	6.7	0.76	.171	6.1	8,950	13.9	2.11	0.54	19.2
59	13	Upper Freeport high-volatile A	900	72.4	13.0	6.1	0.95	.146	5.6	10,100	12.4	2.64	0.41	16.3
59	18	Upper Freeport high-volatile A	900	72.6	12.8	5.9	0.88	.156	5.6	10,100	11.9	2.42	0.37	16.2
60	13	Lower Freeport medium-volatile	800	76.9	11.6	5.7	0.51	.200	3.9	9,050	11.6	1.42	0.36	18.5
60	18	Lower Freeport medium-volatile	800	77.0	12.0	5.4	0.65	.208	3.9	9,350	11.0	1.82	0.34	19.0
60	13	Lower Freeport medium-volatile	900	76.0	12.7	4.9	0.76	.189	3.6	10,450	9.8	2.10	0.17	16.5
60	18	Lower Freeport medium-volatile	900	76.5	12.3	5.0	0.70	.169	4.1	10,350	10.0	2.08	0.23	15.7
61	13	Bell No. 1 high-volatile A	800	68.3	13.7	6.0	1.02	.182	9.2	9,050	12.7	2.88	0.69	22.2
61	18	Bell No. 1 high-volatile A	800	68.3	13.9	5.9	1.02	.206	9.1	9,250	12.2	2.83	0.59	25.9
61	13	Bell No. 1 high-volatile A	900	67.7	14.7	5.5	1.16	.184	9.2	10,300	11.3	3.18	0.43	23.6
61	18	Bell No. 1 high-volatile A	900	68.0	15.5	5.3	1.23	.193	8.7	10,500	10.7	3.36	0.33	22.5

* Coke, tar, ammonia, and light oil are reported moisture-free; gas is reported as stripped of light oil and saturated with water vapor at 60° F and under 30 inches of mercury.

YIELDS OF CARBONIZATION PRODUCTS

TABLE II—Continued

COMPARATIVE YIELDS OF CARBONIZATION PRODUCTS, AS-CARBONIZED BASIS, 13-INCH AND 18-INCH RETORTS AT 800 AND 900° C

Retort Diam- eter No. inches	Bed and Rank	Carbon- izing Temper- ature °C	Yields *					Yields per Ton of Coal *			
			Coke	Gas percent	Tar percent by weight of coal	Light Oil		Tar cubic feet	Gas gallons	In Tar to Gas gallons	(NH ₄) ₂ SO ₄ pounds
						Free Am- monia	Liquor				
62	13	800	69.7	13.9	7.8	0.85	5.7	9,250	2.42	0.82	20.4
62	18	800	69.9	13.9	7.6	0.98	5.7	9,350	2.80	1.02	24.4
62	13	900	69.0	14.9	7.2	0.99	5.5	10,600	2.73	0.57	18.9
62	18	900	69.6	15.0	6.8	1.14	6.2	10,800	3.16	0.65	19.9
64	13	800	78.8	11.1	4.2	0.49	4.9	9,000	1.38	0.42	22.4
64	18	800	78.9	11.2	4.2	0.52	4.5	9,200	1.46	0.40	24.9
64	13	900	78.5	11.9	3.7	0.56	4.2	10,400	1.53	0.18	20.1
64	18	900	78.6	11.9	3.8	0.63	4.6	10,500	1.76	0.28	21.9
13	Average of all coals	800	76.6	12.0	5.0	0.66	4.9	9,080	1.84	0.48	19.6
18	Average of all coals	800	76.7	12.1	4.9	0.69	4.9	9,200	1.94	0.54	21.0
13	Average of all coals	900	76.3	12.8	4.5	0.79	4.6	10,440	2.15	0.30	17.1
18	Average of all coals	900	76.5	12.9	4.3	0.80	4.7	10,540	2.19	0.32	17.3
13	Average of high-volatile A (9 coals)	800	70.5	13.6	7.6	0.88	6.1	9,220	2.47	0.83	21.1
18	Average of high-volatile A (9 coals)	800	70.6	13.6	7.4	0.93	6.3	9,320	2.61	0.94	22.5
13	Average of high-volatile A (9 coals)	900	70.2	14.6	6.8	1.07	6.0	10,570	2.93	0.57	19.1
18	Average of high-volatile A (9 coals)	900	70.5	14.7	6.6	1.08	6.0	10,650	2.99	0.56	19.2
13	Average of medium-volatile (4 coals)	800	78.7	11.3	4.4	0.56	4.2	9,000	1.57	0.34	19.6
18	Average of medium-volatile (4 coals)	800	78.8	11.4	4.3	0.58	4.2	9,160	1.64	0.39	21.2
13	Average of medium-volatile (4 coals)	900	78.4	12.0	3.9	0.68	3.9	10,360	1.86	0.15	16.8
18	Average of medium-volatile (4 coals)	900	78.6	12.0	3.9	0.68	4.1	10,410	1.88	0.23	17.2
13	Average of low-volatile (7 coals)	800	83.3	10.3	2.1	0.43	3.6	8,930	1.17	0.10	17.6
18	Average of low-volatile (7 coals)	800	83.3	10.5	2.0	0.46	3.6	9,070	1.26	0.11	18.8
13	Average of low-volatile (7 coals)	900	83.0	10.9	1.9	0.48	3.2	10,300	1.31	0.05	14.6
18	Average of low-volatile (7 coals)	900	83.0	11.1	1.7	0.49	3.4	10,460	1.34	0.06	14.8

* Coke, tar, ammonia, and light oil are reported as stripped of moisture-free; gas is reported as stripped of light oil and saturated with water vapor at 60° F and under 30 inches of mercury.

Carbonizing temperature probably should be taken to mean the maximum temperature to which the volatile products are exposed after being evolved in the plastic layer. Both temperature and time of contact are factors influencing the extent of secondary decomposition of the so-called primary volatile carbonization products from coal; however, it appears that within the range of industrial carbonization conditions, at least, temperature is the more important.

In the Survey of Carbonizing Properties of American Coals²³ tests have been made at wall temperatures 500, 600, 700, 800, 900, and 1,000° C on more than 60 coals. Charts giving the yields of carbonization products over this range of temperature for a representative high-volatile A coal show that, of all carbonization products, the yield of gas (volume basis) is the most sensitive

to temperature and that of tar next in order. The yield of gas increases more than 500 percent when the temperature is raised from 500 to 1,000° C, and that of tar decreases by about 50 percent. Probably these differences would have been greater had the carbonizing time (time of contact of volatile products) been constant for all tests; actually it varied inversely with the carbonizing temperature. In the course of the survey, tests were also made on some 20 coals at 800 and 900° in retorts of two different sizes; that is, both the carbonizing time and carbonizing temperature were varied independently. The results indicate that the influence on the yields within this range of temperature caused by changing the time about 14 percent is of the order of 1 percent, whereas a change of 100° C (180° F) in the carbonization temperature caused a change in the yields of about 10 percent.

²³ Wilson, J. E., and Davis, J. D., *U. S. Bur. Mines, Tech. Paper 637* (1942), 10 pp.

CHAPTER 23

PRETREATMENT OF COAL FOR CARBONIZATION

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Methods in common use, or proposed, for pretreatment of coals for carbonization include cleaning (see Chapter 16), blending with other coals or inerts, preheating to temperatures below incipient softening, and oxidation at temperatures above normal atmospheric temperatures. Of these four methods only the last two will be considered here.

PREHEATING

The information in the technical literature on the effects of preheating on the yields and qualities of the products, the rates of heating, and the heat economy in the carbonization process is in many respects inconsistent. Some of these factors are complicated by the uncertain direct and indirect effects of removal of moisture from the oven charge. Although preheating has been carried out in full-scale commercial ovens,^{1, 2} it is unfortunate that the results of the tests have not been published, and, therefore, conclusions regarding the possibilities of this modification of normal carbonization practice must be based on indirect evidence.

Parr and coworkers studying Illinois coals

¹ Ramsburg, C. J., Koppers Company, private communication, 1936.

² Litterscheidt, W., *Glückauf*, **71**, 173-81 (1935).

investigated³ the preheating of an Illinois coal to a temperature of 300° C, or "slightly below the point of active decomposition," and charging the preheated material to a retort maintained at a temperature of 700 to 750°. It was claimed that the exothermic reactions that occur at temperatures just above the point of active decomposition maintained a rapid progression of coking through the mass, and that the coke produced was of superior density and strength. In subsequent papers, Parr⁴ emphasized that the reactions that occur below incipient softening of the coal have a profound and, indeed, governing effect upon the reactions that occur at higher temperatures. He called attention to the importance of the time factor in the low-temperature zone and proposed to designate the zone below 300° as the "conditioning" stage of coals for carbonization.

The rapid heating in the second stage of the Parr process has been attributed to an exothermic heat of reaction, estimated⁵ to be equivalent to 36 calories per gram, and not to removal of moisture in the preheat-

³ Parr, S. W., and Layng, T. E., *Ind. Eng. Chem.*, **13**, 14-7 (1921); *Gas Age-Record*, **50**, 531-4 (1922).

⁴ Parr, S. W., *Proc. 1st Intern. Conf. Bituminous Coal*, **1**, 635-49 (1926); *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 54-70 (1928); *Ind. Eng. Chem.*, **21**, 164-8 (1929).

⁵ Chapman, W. R., *Fuel*, **5**, 355-61 (1926).

ing stage. It is difficult to estimate the importance of a heat effect of this magnitude on heating coal over the limited range of 300–350° to 700–750°. The heat of coking in normal carbonization practice has been estimated to range from 325 calories per gram⁶ to more than 600 calories per

ucts. Irregularities in the heating curves obtained during the coking of coals have been attributed to both endothermic and exothermic reactions^{6, 8} and also to experimental error.⁹ A typical heating curve of a coal⁸ is shown in Fig. 1; the departure at about 400° C from the curve calculated

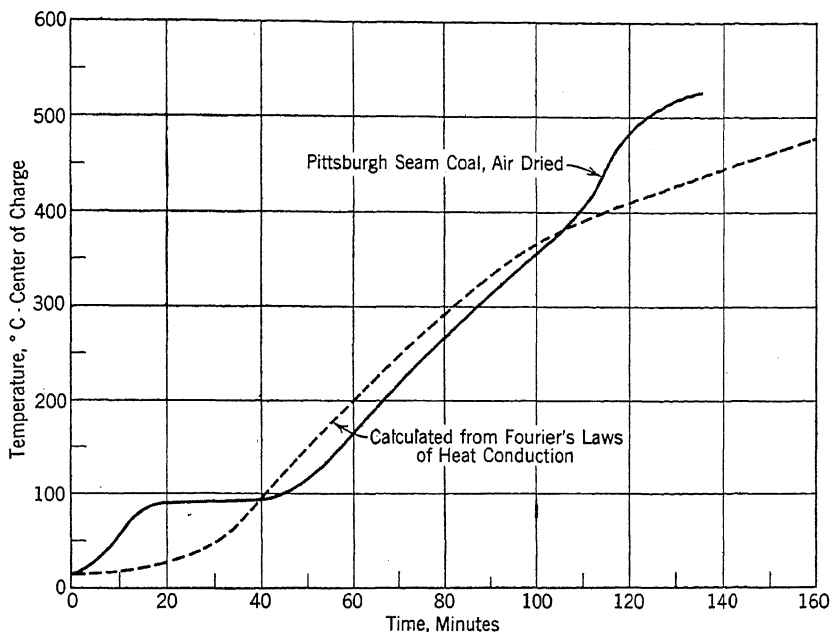


Fig. 1. Typical heating curve of a bituminous coal—cylindrical retort 2.88 inches in diameter.⁸

gram,⁷ depending in part on the operating efficiency of the ovens. In any event, if preheating were of value for use only with coals giving exothermic heats of reaction, it would have limited applicability, for not all coals give positive heats of carbonization, where the heat of carbonization is defined as the difference in heat input to the charge and the sensible heat in the prod-

ucts. Irregularities in the heating curves obtained during the coking of coals have been attributed to both endothermic and exothermic reactions. In general, exothermic reactions are more pronounced in high-oxygen coals,¹⁰ many of which are not adapted to byproduct carbonization; for example, the heats of carbonization of a subbituminous coal from

⁶ Terres, E., and Wolter H., *Gas- u. Wasserfach*, **70**, 15, 30–4, 53–8, 81–5 (1927). Terres, E., and Meier, M., *ibid.*, **71**, 457–61, 490–5, 519–23 (1928). Terres, E., and Voituret, K., *ibid.*, **74**, 97–101, 122–8, 148–54, 178–83 (1931).

⁷ Baum, K., *Glückauf*, **66**, 185–91 (1930).

⁸ Burke, S. P., Schumann, T. E. W., and Parry, V. F., *Proc. Am. Gas Assoc.*, **1930**, 820–55; *Fuel*, **10**, 148–71 (1931).

⁹ Baum, K., and Litterscheidt, W., *Brennstoff-Chem.*, **13**, 386–91 (1932).

¹⁰ Strache, H., and Frohn, E., *Brennstoff-Chem.*, **3**, 337–40 (1922).

Colorado, a noncoking Utah coal, and a Pittsburgh Seam coal were found¹¹ to be approximately 50, 25, and 4 calories per gram, respectively. Davis and coworkers¹² developed a precise method, using an adiabatic twin calorimeter, for measuring heats of carbonization; for a number of representative American coals they obtained values ranging from 37 to -14 calories per gram. On comparison of the calorimetric results with the heating curves obtained by the method of Hollings and Cobb¹³ little connection could be shown between the results of the two series of tests. The heating curves, except for anthracite, showed an exothermic effect from 400 to 750°. Nevertheless, Davis^{12b} concluded that the exothermic heat of carbonization of coal must be a practically negligible proportion of the total heat involved in coking a given coal.¹⁴

If an exothermic heat of carbonization is to be excluded from the causes for the rapid carbonization of preheated coal, a possible explanation may be sought in the

removal of moisture and the thermostating action of water in the center of the charge. This effect is noticeable in Fig. 1. The initial rapid rise in temperature is due to heat convected by water vapor which condenses on the cold coal at the center. The same phenomenon is observed to an enhanced degree in commercial ovens, as is shown in Fig. 2, which reproduces the average coal temperatures at the center of a Koppers oven coking Illinois coal, containing 8.07 percent moisture.¹⁵ Similar curves were obtained at points closer to the oven wall, the temperature rising more rapidly to about 100°C and remaining constant for longer times as the distance from the oven wall increases.¹⁶

It might be expected that removing water from the coal charged to the oven would reduce the coking time about in proportion to the percentage of the total water removed. The evidence on this point is conflicting; Koppers, Baum, and others¹⁷ have claimed on the basis of some theoretical considerations, but largely on the basis of Baum's studies, that up to 6 percent water has no effect on the heat consumption as

¹¹ Burke, S. P., and Parry, V. F., *Ind. Eng. Chem.*, **19**, 15-20 (1927).

¹² (a) Davis, J. D., and Place, P. B., *Ind. Eng. Chem.*, **16**, 589-92 (1924). (b) Davis, J. D., *ibid.*, **16**, 726-30 (1924). (c) Davis, J. D., Place, P. B., and Edeburn, P., *Fuel*, **4**, 286-99 (1925).

¹³ Hollings, H., and Cobb, J. W., *J. Chem. Soc.*, **107**, 1106-15 (1915).

¹⁴ Other studies of the heat evolved or absorbed in coal carbonization, excluding those primarily concerned with thermal efficiency of coke-oven operation, are: Mezger, R., and Müller, M., *J. Gasbeleucht.*, **63**, 669-73 (1920). Strache, H., and Grau, H., *Brennstoff-Chem.*, **2**, 97-9 (1921). Sieben, K., *ibid.*, **3**, 209-11 (1922). Winter, H., *ibid.*, **7**, 117-23 (1926). Niemann, P., *ibid.*, **12**, 386-9 (1931). Baum, K., *Arch. Eisenhüttenw.*, **2**, 779-94 (1929). Feodoroff, V., *Chimie & industrie*, **22**, 231-48 (1929). Terres, E., *Gas- u. Wasserfach*, **72**, 361-9 (1929). Dubois, J., *Gas i Woda*, **11**, 313-7 (1931). Terres, E., Tjia, H. A., Herrmann, W., Johswich, F., Patscheke, G., Pfeiffer, J., and Schwarzmann H., *Angew. Chem.*, **48**, 17-21 (1935). N. N. Norkin, *Coke & Chem. (U.S.S.R.)*, **7**, No. 10, 16 (1937).

¹⁵ McBride, R. S., and Selvig, W. A., *U. S. Bur. Standards, Tech. Paper* **137** (1919), 55 pp.; *Chem. & Met. Eng.*, **21**, 122-8 (1919).

¹⁶ Hilgenstock, R. W., *J. Gasbeleucht.*, **45**, 617-21 (1902). Simmersbach, O., *Stahl u. Eisen*, **34**, 954-8 (1914). Becker, J., *Blast Furnace and Steel Plant*, **10**, 575-83 (1922). Porter, H. C., *Coal Carbonization*, Chemical Catalog Co., New York, 1924, pp. 145-6. Ryan, W. P., *Proc. Am. Gas Assoc.*, **1925**, 861-78; *Fuel*, **5**, 150-7 (1926). Baum, K., *Arch. Eisenhüttenw.*, **2**, 779-94 (1929); *Brennstoff-Chem.*, **11**, 47-51 (1930); *Glückauf*, **65**, 769-77, 812-21, 850-60 (1929).

¹⁷ Koppers, H., *Koppers Mitteilung.*, **14**, 3-8 (1932); *Fuel*, **12**, 139-43 (1933). Baum, K., *Arch. Eisenhüttenw.*, **6**, 263-9 (1933). Dummett, G. A., and Greenfield, G. J., *Gas World*, **100**, Coking Sect., 38-44 (1934). Jäger, H., *Gas- u. Wasserfach*, **78**, 290-3, 308-12, 332-6 (1935). Schläpfer, P., and Rohonczy, G., *Eidgenöss. Materialprüfungsanstalt E. T. H. Zurich*, *Ber.* **102** (1936), 22 pp. See also Baum, K., *Glückauf*, **66**, 185 (1930); *Fuel*, **9**, 492 (1930).

the heat necessary for vaporizing this water can be extracted from the gases moving ahead of the plastic zone. Litterscheidt¹⁸ pointed out that Baum's data are inadequate to justify this position and that if the sensible heat of the gases, whose amount he does not believe to be adequate to carry heat for vaporizing 6 percent of water, was

charge density and moisture content and dependent only on flue temperature and the oven width. The methods of analysis used by Litterscheidt need further investigation and confirmation before they can be generally accepted.

Many observations in the literature on the effect of moisture on coking time are

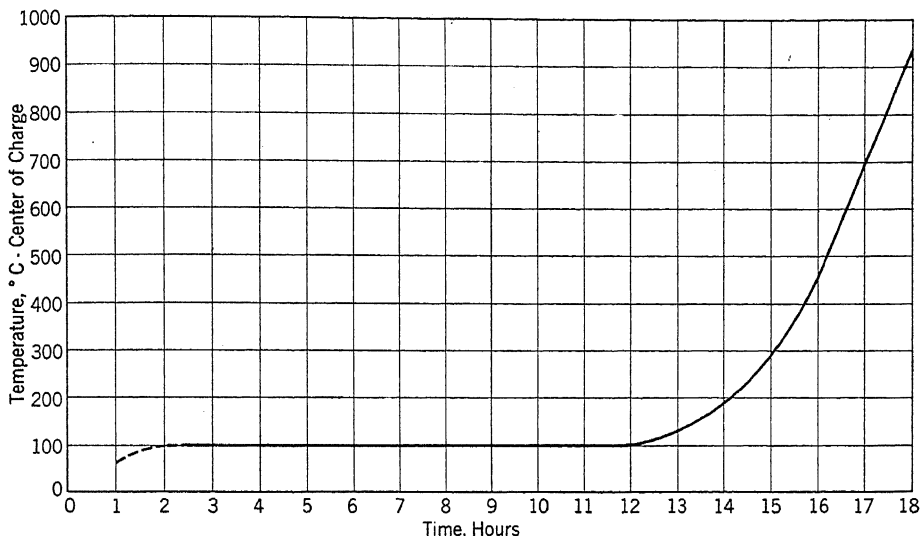


Fig. 2. Temperature at center of 18¼-inch oven charge. Flue temperature, 1,260° C. Normal coking time, 19½ hours.¹⁸

not used for the vaporization it would be used for heating up the coal ahead of the plastic layer. Dubois¹⁹ also did not believe Baum's generalization justified and stated that the fuel requirement increased with increase in water content. In an analysis of data obtained on 18 working coke ovens, charged with coal to a density of 39 to 50 pounds per cubic foot and with moisture contents ranging from 6.5 to 14.1 percent, Litterscheidt¹⁸ found that the coking time was independent of both

in disagreement with the findings of Baum and Litterscheidt. Farnham²⁰ cited a case in which reducing the moisture in the coal charged from 12 to 2 percent reduced the coking time required per oven from 12 hours to 8 hours 40 minutes in a modern battery, and in a 20-year-old battery from 30 hours to 21 hours 40 minutes; the gains respectively in coking capacity were approximately 27 and 38.6 percent. For the same change in moisture content, i.e., from 12 to 2 percent, Dubois¹⁹ found an increase in throughput of 11.3 percent.

¹⁸ Litterscheidt, W., *Glückauf*, **70**, 77-84, 106-12 (1934).

¹⁹ Dubois, E., *Gas- u. Wasserfach*, **81**, 148-51 (1938).

²⁰ Farnham, R. V., *Colliery Guardian*, **149**, 1043-5 (1934).

Mott²¹ has stated that reduction of the moisture content by 5 percent would reduce coking time in a new 18-inch oven from 18 to 16½ hours and in old installations from 32 to 27 hours. Foxwell²² and others²³ have agreed that a decrease in moisture decreases coking time, and Foxwell gave an average of 3 percent increase in the period of carbonization for each percent of added or hygroscopic water. This figure agrees closely with that obtained from an analysis²⁴ of the data of Fieldner and Davis²⁵ on 30 representative American coals ranging in moisture content from 0.8 to 10.1 percent which were carbonized in 13-inch cylindrical retorts at 100° intervals from 500 to 1,100° C. Least-squares solution of the coefficients in the equation

$$CT = a[\text{H}_2\text{O}] + b[\text{FC} + \text{Ash}]$$

where CT is coking time, $[\text{H}_2\text{O}]$ is percent moisture, and $[\text{FC} + \text{Ash}]$ is the sum of the percentages of fixed carbon and ash, gave for the value of a , expressed in percentage of average coking time, 3.26, 3.29, 3.26, 2.85, 3.54, 2.80, and 3.30 at 500 to 1,100° C, with an average value of 3.19 percent increase in coking time for each percent moisture in the charge.

From the above considerations, it would appear definite that, except for possible op-

posing effects, a decrease in moisture, or complete elimination as in preheating, will decrease the time necessary for carbonization of a coal. These possible opposing factors are also functions, generally poorly described, of the moisture content itself. i.e., (1) the rate of heating, (2) the bulk density of the charge, and (3) the ratio of conduction to convection of heat within the charge.

In Fig. 3 are reproduced curves given by Litterscheidt² showing the rise in temperature at the center of an oven charged with a coal preheated to different temperatures. The curve for the untreated coal was not given, nor was the analysis of the coal reported. However, these curves may be compared with the curve in Fig. 2, which is one of the published heating curves for coal in an oven of about the same width and approximately the same flue temperature. The curves in Fig. 3 are not regular in trend, but it may be noted, especially for the coal pretreated at 250°, that although the coking time has been considerably reduced the rate of heating over the temperature interval from the temperature of preheating to 900° is less for the treated than for the untreated coals. The possible effects of this will be discussed in more detail later, but it should be pointed out that the nature of the carbonization reactions depends on the rate of heating and may well influence the heat requirements in such a way that a decrease in moisture may increase the heat required for carbonization under some conditions. Koppers¹⁷ pointed out that, with weakly coking coals, the thermostating action of the water normally present, or sometimes purposely added, is essential for thermostating the coal until such time that a rapid rise in temperature to the plastic stage can occur if coke of satisfactory strength is to be obtained.

²¹ Mott, R. A., *Fuel*, **10**, 424-35 (1931).

²² Foxwell, G. E., *Colliery Eng.*, **7**, 397-9, 438-40 (1930).

²³ Thwaite, A. H., *Gas World*, **72**, Coking Sect., 38-9 (1920). Dubois, E., *Gas-u. Wasserfach*, **71**, 793-8 (1928). Fieldner, A. C., *U. S. Bur. Mines, Rept. Investigations* **3020** (1930), 13 pp. Mott, R. A., and Wheeler, R. V., *Coke for Blast Furnaces*, The Colliery Guardian, London, 1930, p. 210. Dorofeev, D. S., Miroshnichenko, A. M., Senichenko, S. E., and Khadzhinov, V. N., *Coke & Chem. (U.S.S.R.)*, **7**, No. 3, 28-32 (1937). Kustov, B. I., *ibid.*, **8**, No. 14, 38-40 (1938). King, J. G., *J. Inst. Fuel*, **12**, 357, 368 (1939).

²⁴ Lowry, H. H., Landau, H. G., and Nangle, L. L., *Trans. Am. Inst. Mining Met. Engrs.*, **149**, 297-326 (1942).

²⁵ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph* **5** (1934), 164 pp.

Of the many investigations²⁶ of the influence of moisture on the bulk density of coals, perhaps the most thorough of those published are those of Eisenberg and of Stäckel and Radt. Dry coal has the highest bulk density, which decreases to a minimum at 5 to 9 percent moisture depend-

a dry-coal basis, as is shown in Fig. 4.²⁷ It may be seen from the curve that, below about 7 percent, the amount of dry coal per unit volume increases by several percent for each percent reduction in moisture. Since preheated coal is dry, oven capacities might be increased by its use,

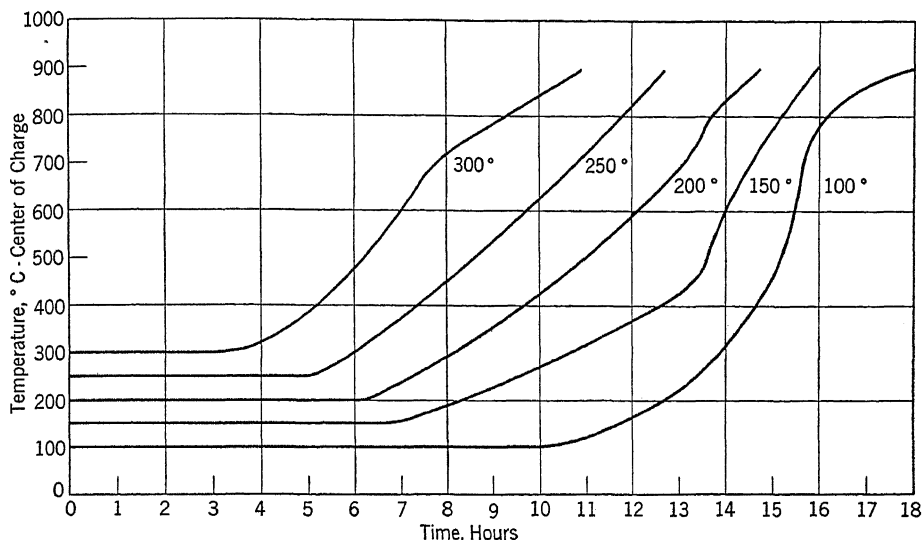


FIG. 3. Temperature at center of 18-inch oven charged with coal preheated to 100, 150, 200, 250, and 300° C. Flue temperature, 1,350° C. Data of Firma Didier.²

ing on the coal and its size distribution. The minimum is generally more pronounced when the bulk density is expressed on a wet-coal basis than when expressed on

unless the increased density and its associated increase in thermal conductivity² increased expansion pressure to a point where damage to the oven walls might follow.²⁸

²⁶ Chapman, H. M., and Barnhart, E., *Iron Age*, **81**, 1440 (1908). Foxwell, G. E., *Colliery Eng.*, **7**, 397-9, 438-40 (1930). Koppers, H., and Jenkner, A., *Glückauf*, **66**, 834-8 (1930); Leven, K., *ibid.*, **67**, 770-2 (1931). Eisenberg, G., *ibid.*, **68**, 445-51, 465-9 (1932). Litterscheidt, W., *ibid.*, **71**, 173-81 (1935). Stäckel, W., and Radt, W. P., *Brennstoff-Chem.*, **15**, 121-6 (1934); *Fuel*, **13**, 282-5, 311-3 (1934). Dummett, G. A., and Greenfield, G. J., *Gas World*, **100**, Coking Sect., 38-44 (1934). Farnham, R. V., *Colliery Guardian*, **149**, 1043-5 (1934). Roberts, J., and Jenkner, A., *International Coal Carbonization*, Sir Isaac Pitman & Sons, London, 1934, p. 49.

²⁷ Russell, C. C., *Koppers News*, October, 1931.

²⁸ Audibert, E., and Delmas, L., *Chimie & industrie*, **17**, 355 (1927); *Fuel*, **6**, 181, 182 (1927). Koppers, H., and Jenkner, A., *Glückauf*, **66**, 834-8 (1930), **67**, 353 (1931); *Fuel*, **10**, 232-9, 273-7 (1931). Altieri, V. J., *Proc. Am. Gas Assoc.*, **1935**, 812-35; *Gas Age-Record*, **76**, 49-54 (1935). Brown, W. T., *Proc. Am. Gas Assoc.*, **1938**, 640-78. Auvil, H. S., and Davis, J. D., *U. S. Bur. Mines, Rept. Investigations*, **3403** (1938), 18 pp. Auvil, H. S., Davis, J. D., and McCartney, J. T., *ibid.*, **3451** (1939), 21 pp. Russell, C. C., *Am. Inst. Mining Met. Engrs., Tech. Pub. 1118* (1939), 14 pp., *Trans.*, **130**, 313-27 (1940).

In this event, preheating might successfully be combined with a controlled oxidation, as described later, to modify the plastic properties and eliminate excessive expansion pressures.

which is furnished by the measurements of pressures developed within the plastic envelope in a cylindrical retort heated on all sides.²⁹ Whether the plastic layer is continuous or not in a full-scale oven is still a

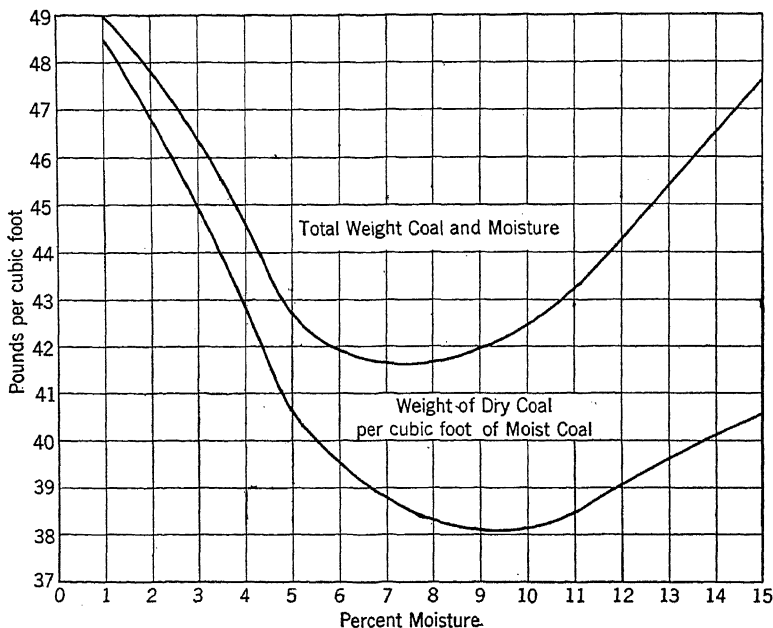


FIG. 4. Weight per cubic foot of coal at various moisture contents.²⁷

According to Litterscheidt,^{2, 13} an increase in bulk density of the coal charged to an oven increases the thermal conductivity of the charge, and also the use of preheated coal increases the thickness of the plastic layer. This increase in thickness of the plastic layer may modify the heat-transfer process in the oven by changing the ratio of the amount of gas released from the coal side of the plastic layer to the amount released from the coke side. The gas released from the coal side contributes to the heat-transfer process by convection of heat to the coal. It is generally agreed that the plastic layer is impenetrable to gases, a convincing proof of

matter of discussion, as is generally recognized in the many papers³⁰ on the path

²⁹ Reynolds, D. A., and Birge, G. W., *Ind. Eng. Chem.*, **32**, 363-7 (1940).

³⁰ Hilgenstock, R. W., *J. Gasbeleucht.*, **45**, 617-21 (1902). Evans, O. B., *J. Gas Lighting*, **124**, 587-91 (1913). Foxwell, G. E., *Gas World*, **S2**, Coking Sect., 56-8, 64-5 (1925), **S3**, 76-7 (1925); *Fuel*, **11**, 4-19 (1932). Forster, W., *Gas World*, **S2**, Coking Sect., 48-52 (1925). Sensicle, L. H., *ibid.*, **S2**, 61-3 (1925). Smith, T. B., *ibid.*, **S2**, 10-2, 38-41, 65-6 (1925). Thau, A., *ibid.*, **S2**, 59-60 (1925). Schmidt, T., *Fuel*, **5**, 486-509 (1926). Petit, T. P. L., *Het Gas*, **46**, 50-1 (1926). Davies, W. E., *Gas World*, **S6**, Coking Sect., 2-5, 12-6 (1927). Damm, P., and Korten, F., *Glückauf*, **67**, 1339-45 (1931). Jäger, H., *Gas- u. Wasserfach*, **78**, 290-3, 308-12, 332-6 (1935). Dubner, E. M., *Coke & Chem. (U.S.S.R.)*, **6**, No. 6, 24-9 (1936). Nikol'skii, N. A., and Stepanenko, M. A., *Khim. Tverdogo Topliva*, **9**, 28-42 (1938).

of flow of gases in a coke oven. It is the amount of gas which leaves the coal side of the plastic layer that determines the amount of heat carried by convection to the coal, and this may be affected by a change in thickness of the plastic layer. Investigators have not agreed on the relative importance of conduction and convection in coal carbonization. Burke, Schumann, and Parry⁸ considered convective heat transfer to be negligible, whereas Foxwell³¹ stated that nearly half of the heat passing into the charge does so by convection of the hot carbonization gases into the colder zones of the oven.

The preceding paragraphs have presented a brief discussion of the probable, and possible, effects of preheating, with complete removal of moisture, on the carbonization process and on coking time. Many questions unfortunately cannot be answered definitely until more data on full-scale commercial trials are made available. It may, however, be stated that the probability is great that preheating will increase the capacity of an oven to a greater extent than the fraction of the total temperature range of carbonization covered by the preheating process.³² This is due not only to the elimination of the present need of removal of moisture in the coke oven, but also to the increased density of the dry, preheated charge. Again it should be pointed out that an increase in bulk density may be harmful to the ovens with certain coals owing to the development of excessive expansion pressures. Even though an increase in oven capacity may in itself be desirable, other considerations must also be taken into account. Some of the questions to be answered are: (1) Is it more economical to dry and preheat coal out-

side an oven than in the oven itself? (2) What difficulties may be expected in charging dry, hot coal to an oven? (3) Will the preheating adversely affect the coking properties of a coal? (4) How will the elimination of moisture from the charge affect the yields and qualities of the products? (5) How will the change in the rate of heating, caused both by elimination of water and the decreased temperature gradient through the charge, affect the yields and qualities of the products? In attempting to answer these questions from published data, it will be evident that the results of different investigators are sometimes directly contradictory.

Koppers¹⁷ has said that there is no heat economy to be gained in drying coal outside the oven. Tramm,³³ on the other hand, claimed that if the drier has only the same efficiency as the oven it takes 48 percent more heat to remove the moisture in the oven on account of the higher exit temperature from the oven. Mott,²¹ in discussing the advantages in removing the water outside the oven, cited tests on a "Universal" drier which showed it to have a net thermal efficiency of 77.1 percent, as compared with efficiencies of 38 to 47 percent for ovens of older design,³⁴ 58 to 68 percent for ovens of modern design,³⁴ or 65 to 75 percent for modern ovens at full output.³⁵ A more recent discussion of the efficiency of driers gives values up to 90 percent net thermal efficiency.³⁶ On the basis of thermal efficiency³⁷ alone it would,

³³ Tramm, H., *Glückauf*, **64**, 719-29 (1928).

³⁴ Davies, R. W., *Coke Oven Managers Yearbook 1926-7*, p. 265.

³⁵ Baum, K., *Fuel*, **9**, 312-37 (1930).

³⁶ Memo. No. 18, *Utilization of Coal Committee, Inst. Min. Engrs., Fuel Econ.*, **11**, 150-3 (1936).

³⁷ Among the many studies of the heat economy of coal carbonization there may be listed: Stewart, E. G., *Gas J.*, **149**, 750-5 (1920). Hollings, H., *ibid.*, **150**, 86 (1920). Chamberlin,

³¹ Foxwell, G. E., *Gas Eng.*, **46**, 367-8 (1929), **47**, 147-8 (1930). See also ref. 2.

³² See also ref. 2.

therefore, appear preferable to dry and preheat coal in a drier rather than in the oven. Relative cost of driers as compared to coke ovens also favors the driers.²⁰ Removal of moisture outside the oven should (1) avoid completely spalling of oven brickwork due to excessive moisture,^{21, 22, 38, 39, 40} (2) reduce the amount of liquor to be handled, evaporated, and to be disposed of as a troublesome effluent,^{21, 22, 38, 39} and (3) assure more uniform operation on fixed pushing schedules due to elimination of variation in moisture content of charge,^{38, 40} all of which represent increased economies.

Coke-oven operators generally emphasize the difficulties expected from charging wet dry coal to an oven. Such coal would be dusty and both a fire and health hazard and a nuisance. When charged to the

oven it might be expected to clog the tar-collecting mains, and, even if it did not, it would increase the "free carbon" in the tar. These objections seem well grounded but might be overcome. The dust might be reduced by oil treatment, which itself is claimed to be of economic value⁴¹ in coke-oven practice, either prior to the drier and preheater or, possibly, in the drier itself. Undoubtedly mechanical systems for handling the hot, dry coal safely could be devised. Another effect of charging dry coal would be an increase of carbon deposits on the oven brickwork.^{7, 22}

Preheating of coal has a marked effect on its plasticity.⁴² The magnitude of the effect depends both on the temperature and on the time of treatment. In some of the reports of experimental work, it seems probable that inadequate precautions were taken to avoid oxidation during the heating period. At 105° C, heat alone has no effect,⁴³ although Schläpfer⁴⁴ reported an appreciable decrease in coking power on heating to 150° for 20 minutes, and, in some experiments, he found a complete loss of coking on heating to 200 to 250° for 15 to 20 minutes. The loss in coking power was attributed to changes in the colloidal structure of the coal and not to oxidation since the heating was carried out in an atmosphere of nitrogen. On the other hand, it has been reported that it takes 4½ hours at 350° to suppress the swelling of coal,⁴⁵

D. S., and McGovern, E. W., *Gas World*, **78**, Coking Sect., 42-4 (1928). Munster, J. K., *Blast Furnace and Steel Plant*, **11**, 389-92 (1928); Wilson, D. W., Forrest, H. O., and Herty, C. H., Jr., *Ind. Eng. Chem.*, **15**, 251-4 (1923). Koch, E., *Gas- u. Wasserfach*, **69**, 971-4 (1926). Still, K., *Glückauf*, **62**, 453-8 (1926); Rummel, K., and Oestrich, H., *ibid.*, **63**, 1809-17 (1927); *Stahl u. Eisen*, **48**, 73 (1928). See Terres, E., and Wolter, H., also Terres, E., and Meier, M., in ref. 6. Hock, H., and Stuhlmann, H., *Glückauf*, **64**, 1445-51 (1928). Peischer, O., *Gas- u. Wasserfach*, **71**, 247-52 (1928). Baum, K., *Arch. Eisenhüttenw.*, **2**, 779-94 (1929); *Brennstoff-Chem.*, **11**, 47-51 (1930); *Glückauf*, **66**, 1424-39 (1930), **68**, 1-8, 40-5 (1932); *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 507-39 (1931). Yushin, V. V., *Domez*, **1931**, No. 4/5, 66-76. Terres, E., and Doermann, O., *Brennstoff-Chem.*, **13**, 221-8 (1932). Foxwell, G. E., *Gas J.*, **208**, 750-1 (1934). Schläpfer, P., and Rohoncz, G., *Schweiz. Ver. Gas- u. Wasserfach, Monats-Bull.*, **16**, 111-5 (1936). Cesari, C., *Chimica*, **13**, 10-1 (1937). Agroskin, A. A., *Coke & Chem. (U.S.S.R.)*, **1939**, No. 2, 19-24. (See also Chapter 21.)

³⁸ Thwaite, A. H., and also Fieldner, A. C., in ref. 23. Glud, W., and Jacobson, D. L., *International Handbook of the Byproduct Coke Industry*, Am. ed., Chemical Catalog Co., New York, 1932, pp. 161-2.

³⁹ Wollenweber, W., *Glückauf*, **57**, 987-92 (1921).

⁴⁰ Schäfer, O., *ibid.*, **63**, 857-67, 1657-8 (1927).

⁴¹ Ramsburg, C. J., and McGurl, G. V., *Proc. Am. Gas. Assoc.*, **1940**, 666-79; *Gas J.*, **233**, 73-6 (1941).

⁴² Seyler, C. A., *Proc. S. Wales Inst. Engr.*, **47**, 9-14 (1931).

⁴³ Longchambon, L., *Compt. rend.*, **204**, 1487-9, 1743 (1937); *J. usines gaz*, **61**, 478-9 (1937).

⁴⁴ Schläpfer, P., *Schweiz. Ver. Gas-Wasserfach, Monats-Bull.*, **11**, 316-29 (1931). See also Schläpfer, P., and Müller, E., *Eidgenöss. Materialprüfungsanstalt E.T.H., Zurich, Ber.*, **55**, 1931, 47 pp.

⁴⁵ Audibert, E., and Delmas, L., *Chimie & industrie*, **17**, 355-66 (1927); *Fuel*, **6**, 131-40, 182-9 (1927).

and that effects on caking power are very small at low temperatures and become important⁴⁶ only at 385°. It has also been reported that a Saar coal of 34.5 percent volatile matter preheated in nitrogen for 2 hours at 250° had a higher coking index than the original coal, but that preheating for 20 hours at 350° or 2 hours at 400° destroyed the coking power completely.⁴⁷ These investigations indicate that there is a safe upper temperature limit for thermal treatment of a coal which is subsequently to be carbonized and that this upper limit is probably above 250° C.

The nature and amount of the different products of carbonization may be expected to be different when coal is charged to the oven both hot and dry owing to the absence of moisture itself and to the change in the rate of heating as indicated in the preceding paragraphs. The specific effects of moisture are not always easily determined. Water vapor is likely to act as a thermal shield to the volatile products obtained in coking, and the recovery of ammonia increases continuously with increase in moisture content of the coal carbonized.^{22, 48} This last fact is true even though only about half the so-called water of decomposition is evolved below the temperature at which tar first appears.⁴⁹ The reduction in the amount of liquor recovered would be greater than calculated from the reduc-

tion in moisture in an amount dependent on the temperature of pretreatment, and the concentration of ammonia in the liquor somewhat less than calculated owing to the shielding effect of water vapor on the yield of ammonia. The effect of moisture on the yield of tar is probably small: Foxwell²² gave data showing an increase in yield from 3.38 to 3.9 percent as the moisture content of the coal increased from zero to 17 percent in agreement with the observation of Seelkopf⁴⁸ but in disagreement with other data in the literature.⁵⁰ Similar lack of accord is found with regard to the yield of benzene.⁵¹ Seelkopf⁴⁸ stated that the pitch content of the tar decreases with increasing moisture in the coal, probably indicating again the action of water as a thermal shield. The coke yield decreases²² slightly as the moisture in the charge increases, is very reactive if much hygroscopic moisture is present,²² and may be softer with dry coal than with undried coal.²⁰ The decrease in coke yield has been attributed to the action of the water vapor on the incandescent coke,^{22, 51, 52} and therefore a small decrease in gas yield would be expected on coking dried coal.

All the effects attributed in the preceding paragraph to moisture, with the exception of those referring to liquor and ammonia, may be counteracted or accentuated by changes in the rate of heating to the final carbonization temperature, either during or after the thermal pretreatment of the coal. Others, besides Parr,⁴ have recognized the importance of the rate of heating through the preplastic range on the subsequent re-

⁴⁶ Pieters, H., and Koopmans, H., *Brennstoff-Chem.*, **13**, 261-4 (1932). See also Brückner, H., *Angew. Chem.*, **52**, 671-6 (1939); Bunte, K., and Imhof, H., *Gas- u. Wasserfach*, **82**, 805-12 (1939); Ginzburg, Y. E., *Coke & Chem. (U.S.S.R.)*, **8**, No. 2/3, 43-9 (1938).

⁴⁷ Bunte, K., Brückner, H., and Simpson, H. G., *Fuel*, **12**, 222-32 (1933).

⁴⁸ Foxwell, G. E., *J. Soc. Chem. Ind.*, **41**, 114-25T (1922). Greenwood, H. D., *Gas J.*, **161**, 750-1 (1923). Börnstein, E., and Seelkopf, K., *Brennstoff-Chem.*, **10**, 357-9 (1929). Seelkopf, K., *Glückauf*, **66**, 989-93, 1029-36 (1930).

⁴⁹ László, E., *Brennstoff-Chem.*, **6**, 221-4 (1925). See also Rau, O., and Lambris, G., *J. Gasbeleucht.*, **56**, 533-7, 557-64, 589-91 (1913).

⁵⁰ Agde, G., and Hubertus, R., *Braunkohle*, **31**, 675-80 (1932). Dorofeev, D. S., et al., *Coke & Chem. (U.S.S.R.)*, **7**, No. 3, 28-32 (1937).

⁵¹ Cf. Börnstein, E., and Seelkopf, K., in ref. 48, with Dorofeev, D. S., in ref. 50.

⁵² Foxwell, G. E., *Gas J.*, **208**, 750-1 (1934).

actions.⁵³ The data of Warren show, for example, that the yields of gas, tar, and coke are determined almost entirely by the rate of heating through the preplastic range. From the previous discussion it seems probable that preheating, combined with drying outside the oven, would mean a slower rate of heating over both the range from 100° to the upper limit of the thermal treatment and the range from this upper limit to the final pushing temperature, the decrease in coking time being due solely to elimination of the long soaking period at the boiling point of water. It might, however, be possible to schedule the pretreatment in such a way that the rate of heating in this temperature range would be more rapid than normal in a coke oven. Although the effect of rate of heating on the coking process is discussed in detail in Chapter 22, a brief résumé of some of the results is necessary here to evaluate the possible value of thermal pretreatment of coal for carbonization.

The work of Warren⁵³ included rates of heating from 0.7 to 21.8° per minute for three "bright" coals—Illinois No. 6, 33.9 percent volatile matter,⁵⁴ Pittsburgh, 33.6 percent, and Pocahontas No. 3, 15.3 percent—and one "dull" coal—High Splint, 36.4 percent volatile matter. The effect of rate on yields was found to be proportional to the logarithm of the rate, i.e., doubling or halving the rate changed the yields by an amount independent of the rate itself, and also to be greater for low-rank than for high-rank coals and for "bright" than for "dull" coals. For the Pittsburgh Seam coal, at 1,000° final temperature, an increase in rate from 1 to 2° per minute increased the tar yield from 3.8 to 4.5 per-

cent and decreased the gas yield from 15.1 to 14.9 percent and the coke yield from 73.2 to 72.7 percent.⁵⁵ Doubling the rate of heating, from 1 to 2° per minute, increased the coke hardness of the Illinois coal about 13 percent, decreased the coke hardness of the Pittsburgh Seam coal about 12 percent, and did not affect the hardness of the other two coals. Mott and Wheeler⁵⁶ have reported that there is an optimum rate of heating for each coal to obtain maximum resistance to shatter and that very slow heating has a more adverse effect on coke strength than very rapid heating. However, since, in their work, the rate of heating was changed by changes in oven flue temperatures, the apparent effect of rate of heating may be due partially to temperature effects. Shimmura⁵⁷ has found that the cell structure of cokes prepared at slow rates of heating is more uniform than that of those prepared at high rates. It has been reported⁵⁸ that fissuring of coke is reduced by slow heating up to about 600° followed by an increased rate of heating above about 700°. Another property of coke affected by rate of heating is reactivity, which increases to a maximum and then decreases as the carbonization rate is increased.⁵⁹ These various investigations would suggest that the yields of gas, tar, and coke obtained from preheated coal would not be very different

⁵³ Cf. Evans, E. V., *Colliery Guardian*, **127**, 737-8, 797-8, 863-4 (1924). Bartling, F., *Braunkohle*, **30**, 348-55 (1931). Jäppelt, A., and Steinmann, A., *Oel, Kohle, Erdoel, Teer*, **13**, 1027-30, 1150-6 (1937); *Braunkohlenarch.*, No. **48**, 22-7 (1937).

⁵⁶ Mott, R. A., and Wheeler, R. V., *The Quality of Coke*, Chapman and Hall, London, 1939, pp. 389-404.

⁵⁷ Shimmura, T., *J. Fuel Soc. Japan*, **9**, 1183-98 (1930).

⁵⁸ Pashkevich, A. Z., *Coke & Chem. (U.S.S.R.)*, **6**, No. 8, 37-43 (1936). Dorofeev, D. S., *ibid.*, **9**, No. 6, 21-5 (1939).

⁵⁹ Müller, W. J., and Jandl, E., *Brennstoff-Chem.*, **14**, 341-7 (1933).

⁵³ Swietoslawski, W., Chorazy, M., and Roga, B., *Przemysł Chem.*, **17**, 25-33 (1933). Warren, Wm. B., *Ind. Eng. Chem.*, **27**, 72-7, 1350-4 (1935), **30**, 136-41 (1938).

⁵⁴ As received basis.

from those from the nontreated coal, owing to the changes in rate of heating that might normally be caused by the use of the preheated coal; the coke might be more uniform in structure and possibly of slightly greater strength.

If the difficulties and hazards of charging hot, dry coal to an oven can be overcome satisfactorily, preheating coal for carbonization should:⁶⁰

1. Increase the capacity of an oven to a greater extent than represented by the decrease in the total temperature interval traversed in the thermal pretreatment. (The decrease in coking time of the heated charge is not due to making use of exothermic heats of distillation but primarily to removal of moisture. The removal of moisture decreases the heat requirement for the charge and also increases the bulk density of the charge—a disadvantageous effect with expanding coals.)

2. Improve the economy of the carbonization process. (It is more economical, both from the standpoint of thermal efficiency and from that of fixed charges, to dry and preheat coal in separate equipment.

3. Reduce the amount of liquor to be handled, evaporated, and disposed of as a troublesome effluent.

4. Not significantly affect the yields of gas, tar, or coke. (The coke should be more uniform in cell structure and strength and might be of improved quality. The yield of ammonia would probably be decreased.)

PRETREATMENT WITH OXIDATION

The changes in caking properties which coals undergo on storage as the result of

oxidation at atmospheric temperatures have been discussed in Chapter 18 and will not be reconsidered here. The changes that take place at low temperatures may be accelerated by raising the temperature of the oxidation process. Several proposals for a combined thermal pretreatment and oxidation at elevated temperatures, particularly for low-temperature carbonization processes, have been made. In the "Carbolux" and "Anthracoke" processes⁶¹ only a portion of the charge is so treated, which is then used as an "inert" filler for the untreated coal. The charge for the "Carbocite" or "Wisner" process,⁶² used by the Pittsburgh Coal Carbonization Company, is subjected in its entirety to the "thermodizing" treatment. In the Carbolux process the charge is heated in narrow, about 12-inch, ovens of the Koppers type with a flue temperature of about 850°, giving a final coke temperature of about 700°. The filler is preheated in rotary driers. The Wisner process, on the other hand, carries out the final carbonization in a rotary retort with a maximum temperature of the external heating gas of 560° and discharges the coke at about 430° C. The cokes made in both processes are very reactive. Insufficient data are available in the literature cited to draw definite conclusions regarding the influence of the combined thermal and oxidation pretreatments on the byprod-

⁶¹ Koppers, H., *J. Inst. Fuel*, **7**, 13-28 (1933). Fitz, W., *Brennstoff-Chem.*, **16**, 345-9 (1935). Ludwig, G., *Arch. Wärmewirt.*, **18**, 77-8 (1937). Deshalit, G. I., and Berman, L. N., *Khim. Tverdogo Topliva*, **8**, 683-92 (1937).

⁶² Wisner, C. B., *Proc. 1st Intern. Conf. Bituminous Coal*, **1**, 800-6 (1926). Brownlie, D., *Trans. Inst. Mining Engrs. (London)*, **71**, 181-239 (1926). Allen, W. H., Jr., *Proc. 2nd Intern. Conf. Bituminous Coal*, **1**, 403-12 (1928). Lesher, C. E., and Archer, A. A., *Chem. & Met. Eng.*, **46**, 343-7 (1939). Lesher, C. E., and Zimmerman, R. E., *Coal Age*, **44**, No. 3, 45-9 (1939). Lesher, C. E., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 328-63 (1940).

⁶⁰ See also Powell, A. R., *Mech. Eng.*, **46**, 389-94 (1924). Roszak, C., *Bull. soc. ing. civ. France*, **51**, 1093 ff (1928). Vol'ison, B. N., *Coke & Chem. (U.S.S.R.)*, **7**, No. 9, 25-8 (1937).

ucts obtained in comparison with those from the untreated coals.

Preoxidation of coal at elevated temperatures not only changes the coking or agglutinating power of coals but also profoundly affects both the yield and qualities of the products obtained on subsequent carbonization.⁶³ Most of the detailed study of Reilly and his associates⁶³ was on a Durham coal of 33 percent volatile matter. This coal did not completely lose its caking power after heating for 2 hours at 300° C. Samples of coal were heated at 185° in a closed system in a current of oxygen, from which the carbon dioxide, carbon monoxide, and water were removed and determined, for periods of time ranging from 0.5 to 115 hours. The total oxygen used, on the basis of the dry coal, ranged from 1.18 to 47.15 percent, although the increase in weight ranged only from 0.32 to 4.37 percent.

These preoxidized coals were subjected to distillation at 600° and the products examined. The yield of gas was a linear

function of the oxygen used; it increased from 2.65 to 17.47 percent by weight of dry, untreated coal, the first figure referring to the yield from the unoxidized sample. The concentration of carbon dioxide and carbon monoxide in the gas increased markedly while that of hydrogen and hydrocarbons decreased. The gas from the untreated coal contained more carbon monoxide than dioxide, but when 20 percent oxygen had been used their percentages became equal and further oxidation increased the content of the dioxide more than that of the monoxide. The water evolved increased from 3.25 to 5.2 percent after 13.2 percent oxygen had been used and then remained constant. The coke yield increased from 77.2 to a maximum of 81.8 percent when about 20 percent oxygen had been used and then decreased to 79.7 percent. The hydrogen content of the coke remained substantially constant; the carbon content increased to a maximum at about 10 percent oxygen used and then decreased; and the oxygen content (including sulfur and nitrogen) remained constant at 9 percent until 13.2 percent oxygen had been used and then increased to 12.9 percent. The coke was very weak in structure after more than 6.44 percent oxygen was used in the preoxidation, corresponding to an increase in the weight of the coal carbonized of 1.69 percent.

As the oxidation progressed the temperature of first appearance of tar increased from 390 to 440°, and the yield of tar decreased continuously but not linearly with total oxygen used from 17.2 to 3.3 percent. Since the amount of tar obtained in these studies was too small for detailed examination, three larger lots (700 to 800 grams) were oxidized until 21.9, 25.3, and 33.5 percent oxygen had been used. The yield of tar, when these larger samples were carbonized to 600°, was smaller, ranging from

⁶³ Kattwinkel, R., *Glückauf*, **63**, 160-5 (1927). Donnelly, J. T., Foott, C. H., Nielsen, H., and Reilly, J., *J. Soc. Chem. Ind.*, **47**, 1-4T, 189-92T (1928). Donnelly, J. T., Foott, C. H., Nielsen, H., and Reilly, J., *ibid.*, **47**, 139-42T (1928). Barrett, W. J., Foott, C. H., and Reilly, J., *ibid.*, **47**, 142-3T (1928). Donnelly, J. T., Foott, C. H., and Reilly, J., *ibid.*, **48**, 38-40T, 101-5T (1929). Rose, H. J., and Sebastian, J. J. S., *Trans. Am. Inst. Mining Met. Engrs.*, **58**, 556-84 (1930); *Fuel*, **11**, 284-97 (1932). Wheeler, R. V., and Woolhouse, T. G., *Proc. 3rd Intern. Conf. Bituminous Coals*, **1**, 406-35 (1931). Le-grave, M., *Chimie & Industrie*, **25**, 18-21 (1931). Pieters, H., and Koopmans, H., *Brennstoff-Chem.*, **13**, 261-4 (1932). Shimomura, K., *J. Fuel Soc. Japan*, **12**, 27-30 (1933). Jäppelt, A., and Steinmann, A., *Oel, Kohle, Erdoel, Teer*, **13**, 1027-30, 1150-6 (1937). Jenkner, A., Kühlwein, F. L., and Hoffmann, E., *Glückauf*, **73**, 213-9, 240-6 (1937). Fieldner, A. C., Davis, J. D., et al., *U. S. Bur. Mines, Tech. Papers* **594**, 43 pp., **596**, 46 pp., **599**, 38 pp., **601**, 45 pp. (1939). Schmidt, L. D., and Elder, J. L., *Ind. Eng. Chem.*, **32**, 249-56 (1940). Schmidt, L. D., Elder, J. L., and Davis, J. D., *ibid.*, **32**, 548-55 (1940).

10.7 to 2.1 percent. Tar acids decreased from 2.38 to 0.15 percent, tar bases from 0.44 to 0.07 percent, the fraction boiling below 120° from 2.01 to 0.73 percent, and the higher-boiling fraction from 9.21 to 1.35 percent. It is unfortunate that samples of tar were not obtained from coal with less drastic oxidation, such, for example, as might be expected in the "thermodizing" pretreatment of the Wisner process. The work is valuable in showing in detail the progressive changes oxidation causes on subsequent carbonization, though the data were obtained for only one coal.

Studies similar to those of Reilly and associates have been reported by Davis⁶³ and coworkers on seven American coals ranging from 39.6 to 18.0 percent in volatile matter, on a mineral-matter- and moisture-free basis. In this work the oxidation was carried out largely at 99.3° C and, in general, only until 1.5 to 2.5 percent of oxygen by weight of the dry, mineral-matter-free coal had been consumed. The carbonizations were carried out at 800° in cylindrical retorts holding 80 kilograms of crushed coal following the BM-AGA method²⁵ and in some cases in a smaller retort with a byproduct recovery train.⁶⁴

For all the coals tested the yields of tar decreased rapidly with oxidation, the average decrease for 1 percent oxygen consumed being 16 percent of the average yield. The decrease in tar yield appeared to be the most sensitive property for indicating the extent of oxidation of the coals. In agreement with the work of Reilly it was found for four of the coals that the yield of tar acids decreased more rapidly with oxidation than the yield of tar. The yield of total aromatics in tar and light oil decreased more slowly with the oxidation of each coal than the yield of tar plus light oil. Where

the yield of naphthalene and anthracene was low from fresh coal, oxidation increased the yield rapidly, and, where the yield from fresh coal was high, oxidation decreased it. In general, the tars made from oxidized coals tended to show a somewhat increased content of pitch.

Except for the highest-rank coal, the yield of gas increased approximately proportionally to the amount of oxygen consumed; the increase was not large and was attributed to increased evolution of oxides of carbon, chiefly the dioxide. The yields of liquor increased rapidly with oxidation of the coals, the rate of increase being particularly great for the higher-rank coals. Yields of ammonia showed a definite increase with oxidation of all but one coal.

For each percent oxygen consumed, the yield of coke increased about 0.3 percent of its average yield. In general, the coke from coals slightly oxidized had smaller pores or finer structure, but further oxidation resulted in poor fusion or pebbly coke in which the outlines of the original coal particles could be seen. For all the coals tested, oxidation increased the apparent specific gravity of the coke formed. Coke strength as measured by tumbler and shatter tests increased slightly to a critical value and then decreased rapidly with further oxidation. It was found that the sum of the oxygen in the fresh coal plus the amount of oxygen consumed in decreasing by 20 percent the hardness (percent retained on 0.25-inch screen after the tumbler test) of the coke was linearly related to, and increased with, the percentage of volatile matter of the coal on a dry, mineral-matter-free basis.

From the above discussion, thermal pretreatment combined with oxidation of a coal may, under controlled conditions, be used to modify its caking properties and, if the oxidation is not carried beyond a

⁶⁴ Schmidt, L. D., Elder, J. L., and Davis, J. D., *Ind. Eng. Chem.*, **28**, 1346-53 (1936).

critical, and generally small, amount, an improvement in quality of the coke may be achieved. The yield of coke and gas would be somewhat greater and the yield of tar somewhat less than obtained from carbonization of unoxidized coal. The increased yield of gas would be chiefly carbon

dioxide, which would both increase the gas density and decrease its heating value. The "thermodizing" of coal has not had wide adoption in the carbonization industry but is used commercially in the processes referred to in the first paragraph of this section.

CHAPTER 24

THE PHYSICAL PROPERTIES AND REACTIVITY OF COKE

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For many years about 15 percent of the total annual coal production of the nation has been coked. Most of the coke produced is used in blast furnaces for the production of pig iron, but the proportion of the tonnage so used steadily declined from World War I to 1938; in 1940, however, it represented 74.5 percent of the total production. The remainder was used as foundry coke, for smelting the nonferrous metals, in the manufacture of water gas, in miscellaneous other industrial uses, and in domestic heating. Additional data are shown in the annual reviews published by the United States Bureau of Mines, some of which are given in Table I.¹ In addition to coke from coal produced in beehive and byproduct ovens, nearly constant quantities of gas-house coke, about 750,000 tons in 1940, and about 1,500,000 tons of petroleum coke were also produced in 1940.

It is evident that the blast furnace is still the most important single consumer of carbonized fuel, but other uses, especially as a smokeless household fuel, are becoming of considerable importance. Although the quality of coke is of fundamental importance for its use in blast furnaces and the foundry cupola, it is less significant for

other purposes; thus, as the latter grow by comparison with the former, it is quite possible that emphasis on the characteristics of the coke may become less pronounced. It appears to be true that it is only in those applications in which the quality of a material of commerce, such as pig or cast iron, is directly affected by the quality of the coke, that much stress is laid on this characteristic; where coke quality affects merely the efficiency and, hence, a portion of the cost of operation, it tends to be subordinated to considerations of price.

In general, quality testing is a practice of long standing in the coke-using trades. The A.S.T.M. specification for foundry coke dates back to 1916, making it, with the method for sampling coal, the oldest standard included in the 1938 Edition of Standards on Coal and Coke. There has been great activity in the elaboration of tests for the various properties of coke that have, at one time or another, been considered to be important; although a few tests have been standardized and employed extensively enough in the standard forms so that they may be classed as accepted, many of the properties may be evaluated by, literally, dozens of methods. In the first class is the shatter test, and to a smaller degree the tumbler test, as used

¹ Shore, F. M., Otero, M. M., and Cooke, M. F., *Minerals Yearbook, Review of 1940*, U. S. Bur. Mines, 1941, pp. 855-902.

TABLE I
COKE PRODUCTION AND CONSUMPTION¹

	1923		1936		1937		1938		1939		1940		1941	
	Thousand Net Tons	Per- cent	Thousand Net Tons	Per- cent	Thousand Net Tons	Per- cent	Thousand Net Tons	Per- cent	Thousand Net Tons	Per- cent	Thousand Net Tons	Per- cent	Thousand Net Tons	Per- cent
Production, total	56,978	100	46,275	100	52,375	100	32,495	100	44,325	100	57,072	100	65,186	100
Beehive	19,380	34.0	1,706	3.7	3,165	6.0	837	2.6	1,444	3.3	3,058	5.4	6,704	10.3
Byproduct	37,598	66.0	44,569	96.3	49,210	94.0	31,658	97.4	42,882	96.7	54,014	94.6	58,482	89.7
Consumption, calculated	55,173		47,052		51,272		31,063		44,953		57,026		65,374	
Furnace coke, including other coke used at B.F. plants	47,774	86.5	30,772	65.3	36,752	71.7	19,070	61.4	31,499	70.1	42,484	74.5	50,455	77.2
Foundry coke	3,601	6.5	1,922	4.1	2,039	4.0	1,216	3.9	1,632	3.7	2,090	3.7	2,846	4.4
Industrial coke (including water gas)	2,284	4.1	2,033	4.3	3,829	6.5	2,787	9.0	3,193	7.1	3,582	6.3	4,225	6.5
Domestic coke	2,733	4.9	10,021	21.3	8,108	15.8	7,223	23.3	7,638	17.0	8,231	14.4	6,683	10.2
Unaccounted for		-2.0		5.0		2.0		2.4		2.1		1.1		1.7

in the United States and Great Britain. In the second class are such tests as reactivity, true and apparent density, combustibility, adsorptivity, electrical conductivity, and compression strength. Many of these tests are of rather doubtful significance; some may be of the first importance for single uses but of no value for any other purpose; still others appear to be merely duplicate methods for the determination of significant properties that may be measured directly in other ways. It will appear that adequate tests are available for almost every physical characteristic of coke that can be imagined; but the significance of the various properties for specific purposes and their dependence on the characteristics of the coal and the carbonizing process employed are not generally recognized. Apparently, the most urgent present need is for the correlation of the results of tests made by the various available methods on well-characterized cokes with the results of operations in which these cokes are utilized. Such correlation may be expected to show which properties of coke are significant and which are of no importance for any particular application.

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In order to estimate the suitability of a coke for its use in the blast furnace or cupola it is necessary first to set up criteria defining satisfactory performance. Such criteria are furnished by the common operating characteristics: (1) the rate of production attainable in, say, tons of iron per hour, day, or week; (2) the economy of operation, given by the coke rate of a blast furnace in pounds of coke per ton of iron produced; and (3) the quality of the product, which is usually given by the analysis of the iron and, sometimes, the iron temperature. Additional criteria may

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be added to this list to suit the circumstances, but once the operating criteria are known and accepted, the suitability of any coke should be considered only on the basis of its effect on the recognized criteria. Too often, in this as in other fuel-using processes, a particular fuel has been condemned merely because it led to a condition unfamiliar to the operator, not because it actually made any perceptible change in the criteria of operation. It is desirable, then, to determine whether any correlation exists between the criteria of operation listed above and the quality of the coke as determined by the values of measurable quantities characterizing its physical properties.

The quantities to be considered may be classified into three groups: in the first are the criteria of the quality of operation mentioned above, which may be considered to be the dependent variables of the problem. It is desirable to discover their dependence on quantities of the second group, the physical properties of the coke, which may be controlled as such, and which, therefore, may be considered independent variables. But, in addition to these two groups, there is a host of other quantities which from one point of view may be considered as dependent variables, but from another behave like independent variables since their changes cause changes in the values of the dependent variables. Though there may be a functional relation between the dependent and the independent variables, this relation is not direct, but comes about by the influence of the independent variables on those of this third group which, in turn, control the dependent variables directly. Thus, the variables of the third group may be called the "intermediate" variables; or, since they are those, such as temperature, temperature distribution, and void volume of the stock

column, which are commonly controlled in laboratory, though not in practical investigations, they may also be classified as "fundamental" ones. Their changes are not of immediate interest in themselves but merely as indicators of the mechanism by which a change in the independent variables effects a change in the dependent ones.

It may be possible to predict the overall change in the product from the results of laboratory investigations, if the changes in all the "intermediate" variables resulting from a given change in the independent variables are known. This condition, however, is seldom satisfied in the observation of commercial processes, so that it may be more economical to suspend observation of the intermediate variables and observe the effect of changes in the controllable quantities on the overall operation. It should be noted that the classification given above is not absolute; thus, though the temperature is mentioned as one of the intermediate variables, the temperature at a given point, as for instance that of the iron at tapping, may be one of the criteria of operation, that is, one of the dependent variables.

The correct evaluation of blast-furnace coke is still an unsolved problem.² It has been said that this is not because the blast-furnace manager does not know exactly the type of coke he wants, but rather that no definite specification exists which will define exactly the properties he requires.³ Although shatter and tumbler tests are made regularly in many plants, the shortcomings of such tests are well recognized.²

Variations in the silicon and sulfur contents of the iron occur without any *known*

² Joseph, T. L., *Blast Furnace Steel Plant*, 26, 47-52 (1938), especially p. 49.

³ Evans, E. C., *Gas World*, 84, Coking Sect., 6-11 (1926). See also Nicol, E. W. L., *Coke and Its Uses*, Benn Bros., London, 1923, 134 pp.

change in practice or materials both in blast-furnace and foundry plants. This indicates that the processes considered are not "controlled,"⁴ so that variations in the quality of the product may occur from no known cause even when practice apparently remains the same. That this is indeed true for some coke-oven plants, at least, is confirmed by the analysis of data from a certain plant⁵ where the resistance of the coke to shatter took on three different values in different portions of a 6-month period during which no change of practice was known to have occurred.

In the regular operation of blast furnaces, "Johnson's critical temperature theory, or the concept that the temperature attained in the crucible is of paramount importance, seems to fit the known facts of practice best. In the operation of furnaces day in and day out . . . operators adjust the burden to meet silicon and sulfur requirements."⁶ Thus, if the silicon and sulfur contents of the iron are determined by the basicity of the slag and the crucible temperature, the desired metal specification will be met by adjusting the burden to give the proper iron temperature when operating with a more or less constant slag. That this is so is shown by data from several hundred casts⁷ and by work on foundry cupolas⁸ showing that the quantity ($C + 0.3 \text{ Si}$) is nearly a linear function of hearth temperature. The chemical reactions leading to this dependence of iron

analysis on hearth temperature are known; in fact, the equilibrium constants for many of them have been calculated,⁹ and they show such variations with temperature that the changes noted above may be understood as approaches to the equilibrium concentrations. This leads to the conclusion that only such properties of the coke will be important in determining the quality of the iron as affect the temperature in the crucible. This, of course, does not mean that such characteristics as the ash content and composition need not be controlled; even though it is true that the burden can be adjusted so that any ash will enter the slag to give a product of the desired basicity, and enough coke can be fired to give the required temperature regardless of its carbon content, these adjustments cannot be made to match random or sudden fluctuations, so that it is essential that the ash content and composition vary only slowly.¹⁰

The temperature in the crucible of the blast furnace or in the hearth of the cupola is greatly dependent on the temperature attained as the result of combustion at the tuyères, but it may also be influenced by the thermal conductivity of the slag and the magnitude of heat losses from the hearth. Though the literature holds little information on this point, in one report¹¹ there was an increase in temperature of 100° C from the first iron tapped, i.e., that from the bottom of the crucible, to the last, and the slag was said to be about 50° hotter still. Similarly, Kinney, Royster, and Joseph¹² found that, at the

⁴ Shewhart, W. A., *Economic Control of Quality of Manufactured Product*, D. Van Nostrand, New York, 1931, pp. 1-7.

⁵ Unpublished data. Work in progress in the Coal Research Laboratory.

⁶ Joseph, T. L., *Blast Furnace Steel Plant*, 27, 60-6, 175-9 (1939).

⁷ Joseph, T. L., *Trans. Am. Inst. Mining Met. Engrs.*, 125, 204-45 (1937).

⁸ Johnson, H. V., and MacKenzie, J. T., *Trans. Am. Foundrymen's Assoc.*, 44, 178-90 (1936).

⁹ Darken, L. S., *Trans. Am. Inst. Mining Met. Engrs.*, 140, 204-21 (1940).

¹⁰ Gill, C. S., *J. Iron Steel Inst. (London)*, 116, 91-7 (1927).

¹¹ Bohm, I., *J. Iron Steel Inst. (London)*, 116, 83-7 (1927), especially p. 85.

¹² Kinney, S. P., Royster, P. H., and Joseph, T. L., *U. S. Bur. Mines, Tech. Paper* 391 (1927), 65 pp.

level of the tuyères, the temperature varied from 1,530° at the inwall to 1,250° at the center of the plane; the temperature of the slag was 1,409°, and that of the metal (average?) was 1,385° C.

On the assumption that the combustion temperature was the important variable, however, and in the belief that the combustion temperature increased with the reactivity of the coke, there has been, since 1921, a search for a correlation of coke reactivity with iron quality and the rate of iron production,¹³ along with a demand by some blast-furnace operators for a reactive coke. The belief that combustion temperature increases with coke reactivity, however, is in error, because in the blast furnace, where the fuel is burned to carbon monoxide within a very short distance of the tuyères,¹² only the heat of combustion of carbon to carbon monoxide is available, and this is independent of the reactivity of the coke. If, however, the maximum temperature attained anywhere in the combustion zone is the significant quantity, unreactive coke is to be preferred to reactive coke, since, as found in cupola investigations,^{14, 15} the maximum temperature attained increases with a decrease in the reactivity of the coke. This results also from theoretical considerations,¹⁶ from which it may be deduced that the maximum temperature is higher the greater the ratio of the rate of the reaction $C + O_2 = CO_2$ to the rate of the reaction $C + CO_2 = 2CO$. At the temperature of the hearth, the rate of the first reaction may be ex-

pected to be independent of any chemical characteristic of the coke,¹⁷ whereas that of the second might still be increased by an increase in coke reactivity, thus leading to a smaller value of their ratio and hence a lower maximum temperature. Finally, it has been shown that the volume of the combustion zone in the blast furnace depends only on the size of the coke and on the velocity of the blast,^{12, 18} so that, apparently, the combustibility or reactivity of the coke does not materially affect the course of the combustion reactions, suggesting that it may not affect the temperature in the hearth. On the other hand, the conclusion that high hearth temperature is favored by the use of unreactive coke is supported by Melzer,¹⁹ who found that the frequency of casts having low silicon from blast furnaces making merchant iron increased when the reactivity increased as indicated by a drop in ignition temperature.

Apparently the demand for a reactive coke is based not only on the desire for high hearth temperatures but also on the need for some property, usually referred to as easy combustibility, which determines the rate at which the furnace melts iron by determining the rate at which the blast can be supplied. When the increase in blast pressure required to produce a given increase in rate of blast is large, it is said that the coke is hard to burn, or difficulty is encountered due to hanging or slips; where it is low, the furnace is said to "take the air easily" and the coke is said to be easily combustible. Obviously, such behavior as this is in no way related to the chemical reactivity of the coke but depends on the permeability of the stock

¹³ Koppers, H., *Stahl u. Eisen*, **41**, 1173-81, 1254-62 (1921).

¹⁴ Braunholtz, W. T. K., Nave, G. M., and Briscoe, H. V. A., *Fuel*, **8**, 428-37 (1929).

¹⁵ Blayden, H. E., Noble, W., and Riley, H. L., *J. Iron Steel Inst. (London)*, **130**, 25-44P (1937).

¹⁶ Mayers, M. A., *Trans. Am. Soc. Mech. Engrs.*, **59**, 279-88 (1937).

¹⁷ Mayers, M. A., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 408-24 (1938).

¹⁸ Perrott, G. St. J., and Kinney, S. P., *ibid.*, **69**, 543-84 (1923).

¹⁹ Melzer, W., *Glückauf*, **66**, 1565-76 (1930).

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column to gas flow. So far as this depends on the coke alone, the permeability will be increased by an increase in the void volume of a bed of the coke, which, in turn, is increased by uniformity of size of the coke and by irregularity of the shapes of the pieces.

Thus, the question of combustibility appears to be one, not of the chemical nature of the coke, but of its physical properties; more especially of such structural properties as shape, size, and resistance to shattering and abrasion. This conclusion is supported by the results of tests on a blast-furnace plant,²⁰ which showed that a saving of about 4.5 percent in the coke supplied to the plant could be secured by removing the breeze below 1¼ inch from the coke supplied to it. This permitted a decrease in coke charged to the furnaces of nearly 10 percent with the net saving quoted above, allowed an increase in blast temperature of more than 100°, and made for more regular operation of the furnace. The removal of breeze decreased the size range of the coke supplied to the furnaces, thus increasing the volume of voids in the stock column and, hence, its permeability. Moreover, foundry trials^{14, 21} have shown that equally good performance can be obtained with cokes of different sizes provided that the sizing is close, so that high permeability of the bed is retained. On the other hand, Bowers and MacKenzie²² have shown that coke size may have specific effects on cast-iron analysis, and it appears that the permissible variations in coke size for any cupola are limited by the

cupola diameter and the operating practice.^{14, 23}

It is evident that, so far as the reactions in the hearth are concerned, the permeability of the stock column to gas flow is the most important characteristic since it determines the possible rate of air flow through the tuyères for a constant blast pressure. The question arises whether the reactions in the upper part of the column place any additional demands upon the coke beyond those required to produce an open bed. It has been shown^{12, 24, 25} that, in moderately rated furnaces, a large portion of the reduction of the ore takes place at levels in the stack above the bosh where the temperature is not above 850° C. At temperatures below this, the rate of the reaction $C + CO_2 = 2CO$ is very small, and even a doubling of the reactivity of the coke would have only a small effect on the gas composition; in fact, at somewhat higher levels and lower temperatures the reaction actually is reversed, with the deposition of carbon.^{12, 26} Moreover, from this level downward, the temperature increases very rapidly, so that the region at temperatures between 850° and 1,100° is rather small. This region, however, is the only part of the column in which a difference in coke reactivity can make any appreciable difference in the gas composition, since above 1,100° the reaction rate is limited by physical factors and does not depend on the reactivity of the coke. Hence, the most that any coke can do is to supply a gas containing a negligible amount of car-

²³ Mulcahy, B. P., *Fuel*, **18**, 100-9 (1939).

²⁴ Kinney, S. P., *U. S. Bur. Mines, Tech. Paper 397* (1926), 22 pp.; Bone, W. A., et al., *Iron Steel Inst. (London), Special Rept. 18* (1937), 98 pp.

²⁵ Kinney, S. P., *U. S. Bur. Mines, Tech. Paper 459* (1930), 92 pp.

²⁶ Wüst, F., *J. Iron Steel Inst. (London)*, **116**, 65-77 (1927).

²⁰ Marshall, D. F., and Wheeler, R. V., *J. Iron Steel Inst. (London)*, **127**, 87-113 (1933).

²¹ Wagner, A., *Stahl u. Eisen*, **45**, 929-35 (1925). Hollinderbäumer, W., *Giesserei*, **22**, 73-5 (1935).

²² Bowers, J. A., and MacKenzie, J. T., *Trans. Am. Foundrymen's Assoc.*, **45**, 293-319 (1937).

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bon dioxide at the 850° level; the gas composition at higher levels cannot be materially influenced by the reactivity of the coke. If, however, almost all the reduction has already taken place by the time the stock reaches that level, there is little reduction for the gas to do at lower levels so that there will be little production of carbon dioxide, and almost any coke, regardless of reactivity, can supply gas containing not more than a few percent of this constituent at the 850° level.

The behavior just described was not so clearly shown in the investigation of a furnace driven at a high rate,²⁷ a result that may have been associated with the high rate of driving, but which may also have been due to the extreme channeling of the stock column. In this furnace, only 24 percent of the reduction took place above a level 24 feet above the tuyères, where the temperature was 940°; but it should be noted that this level was 5 feet or 26 percent further above the tuyères than in the other furnaces investigated, although the height of this 700-ton furnace, from tuyères to stock line, was only 1 percent greater than that of the other furnaces. Furthermore, the differences in percent reduction and gas temperature at this level between this and the lower-rated furnaces may be more apparent than real because of the difficulty in integrating over such nonuniform distributions as were found in this furnace. In this connection, it should be noted that the largest part of the gas passing this level went through a region where the temperature was only 740°.

This analysis is supported by the fact, recognized since 1917,²⁸ that the amount of coke oxidized in the stack per ton of iron is

²⁷ Kinney, S. P., *U. S. Bur. Mines, Tech. Paper* 442 (1929), 148 pp.

²⁸ Richards, J. W., *Trans. Am. Inst. Mining Met. Engrs.*, 56, 372-5 (1917).

nearly independent of the coke rate or other factors. Thus, it seems likely that the rate of production of a furnace is not limited by the rate of reduction of the ore, but by the rate of melting of the reduced iron; there appears to be ample length of stock column so that the burden is exposed to reducing gas at a high enough temperature for reduction to be practically complete before the stock reaches the zone of high temperature below the bosh. Although this conclusion may be questioned for furnaces driven at very high rates,²⁷ the considerations outlined above suggest that it may also hold true for them when operated with more uniform gas flow than in the one described by Kinney. If this should be so, it is evident that differences in reactivity of the coke can have little or no effect on the completeness of the process, and that the principal function of the coke in the stack is to provide an open and porous structure supporting the burden so that it is effectively exposed to the action of the reducing gas.

Further confirmation of the conclusion that the resistance to gas flow of the stock column is of the greatest significance in determining the economy and rate of operation of a blast furnace may be obtained from work²⁵ in which a material reduction of coke consumption, with a marked increase in the rate of production attainable, was secured by sizing the ore charged to the furnace and charging the different-size fractions in separate layers. The results appear in Table II, in which the column headed "A" shows the results of normal operation with unsized ore; that headed "B," the results with the ore divided into a coarse and a fine fraction, each fraction being charged separately; and that headed "D," the results of operations with the ore divided into fine, intermediate, and coarse fractions. It is evident that the effect of

TABLE II

EFFECT OF CHARGING SIZED ORE ON BLAST-FURNACE OPERATION²⁸

Period	A	B	D
Number of ore sizes charged	1	2	3
Foundry iron			
Average output, tons per day	280	337	360
Coke consumption, pounds per ton	2,713	2,402	2,225
Basic iron			
Average output, tons per day	314	376	396
Coke consumption, pounds per ton	2,457	2,122	2,042

charging the different-size fractions separately must be to increase the permeability of the column, since it sets up layers in each of which the size range is smaller than with unsized ore, thus leading to an increase in the volume of voids in the layer.

It is evident that a coke containing a wide range of sizes will have some sizes which fill up the space into which the ore would normally sift, so that it will become necessary to increase the ratio of coke to ore in order to provide enough space for the burden. That the ore does sift down into the interstices between pieces of coke, at least the finer parts of it, is suggested by the fact that none of those^{24, 27} who have extracted samples of solids from the stock column have mentioned any evidence of layering, and by the fact that estimates of the void volume of the stock column based on measurements of the gas velocity by means of a Pitot tube²⁹ have given values of the order of 9 percent. This is just the value that would be calculated if a small-sized ore having a void volume of 30 percent when bedded alone were used to fill the interstices between large pieces of coke, which, when bedded alone, has a void vol-

ume of 30 percent. It is perhaps not generally realized how closely related are the void volume in a bed of coke and the values of coke rate per ton of iron that are commonly observed. If the interstices of a coke bed having 30 percent voids were filled with a burden having an average density of 275 pounds per cubic foot and containing 48 percent iron, the ratio of coke to iron in the mixture would be 2,490 pounds per ton. If the void volume of the coke were increased to 40 percent, for example by more careful sizing, the ratio of coke to iron in a mixture prepared in the same way would be 1,590 pounds per ton.

It has been estimated that, under normal operating conditions, the pressure gradient of the blast supports about 50 percent of the weight of the stock.³⁰ It is evident that, if the net void volume under normal conditions is only 9 percent as noted above, it would take only a very small decrease in void volume to raise the pressure gradient to the point where it would support the entire weight of the stock and prevent its normal downward movement in the furnace. It seems likely that this is the cause of "hanging," and that "slips" occur when the pressure under such a relatively impermeable layer is suddenly released by the development of a channel through the layer. Thus, it is evident that marked irregularity of the gas flow in a furnace, which is recognized in practice³¹ as a symptom of poor operating conditions, results from insufficient free space in the stock column for the passage of gas and can be corrected either by increasing the ratio of coke to burden, which is the usual procedure, or alternatively, by increasing the void volume of the coke charge by more rigid sizing.

³⁰ Furnas, C. C., and Joseph, T. L., *U. S. Bur. Mines, Tech. Paper 476* (1930), 73 pp.

³¹ Johnson, H. W., *Blast Furnace Steel Plant*, 26, 590-4, 689-93 (1938).

²⁹ See pp. 71-2 of ref. 27.

The foregoing discussion indicates that the structural properties of coke are of the greatest importance in determining blast-furnace properties but does not indicate which ones of that class are significant. Only one method seems to be available for the determination of the significance of individual criteria of coke quality, namely, direct comparison of results of tests with records of furnace operation. This method, however, is difficult of application because of the great number and variety of factors which affect the operation. It appears to be quite impracticable to maintain all other factors but the one investigated constant over a long enough period of time to secure significant results. Thus, it is necessary to apply the methods of statistics to the records of operation and of coke quality, in the hope that correlations³² may be found among the most significant of the numerous variables concerned. Not many published data are available with which to try such an attempt at correlation. Perhaps the most satisfactory for this purpose are those presented by Brooke, Walshaw, and Lee³³ before the British Iron and Steel Institute, consisting of weekly average values of twelve quantities related to furnace operation or coke quality, given graphically for all or part of a period of 1 year and 7 months.

Statistical correlation of these data³⁴ indicated that the production rate was significantly related to the shatter test or to the Cochrane drum test; that the coke rate depended on the shatter index, the produc-

tion rate, and the blast temperature; and that, during a portion of the test, the silicon content of the iron depended on the shatter index. The shatter index of the coke was shown to depend on the Sheffield Swelling Index of the coal and its fineness as charged to the ovens. It is recognized that the results are of illustrative value only because of shortcomings of the data for use in such statistical analysis; in particular, the raw materials and methods of operation are quite foreign to American practice. The analysis was shown, however, to be capable of dealing with the extremely complex problem of blast-furnace operation.

The discussion of foundry and blast-furnace cokes above may be summarized by the following conclusions, which are probably true but require additional data for their substantiation.

1. The structural properties of coke, which determine the size of the pieces and the void volume in a bed of the coke as charged into the furnace, are of prime importance in determining the performance of either the cupola or the blast furnace.

2. The reactivity of coke is probably significant for foundry practice, a coke of low reactivity being desirable to produce high hearth temperature and to minimize solution loss.

3. Further correlation of coke properties with the results of furnace operation by statistical methods is essential for the determination of which of the many tests available for characterizing cokes are of special significance with respect to the economy and capacity of any particular operation.

COKE FOR GAS PRODUCERS AND COMBUSTION EQUIPMENT

The use of coke as fuel for gas producers and generators and for heating has been, until recently, largely a means for dispos-

³² Fisher, R. A., *Statistical Methods for Research Workers*, Oliver and Boyd, Edinburgh, 1936, 339 pp.

³³ Brooke, W. J., Walshaw, H. R. B., and Lee, A. W., *J. Iron Steel Inst. (London)*, **134**, 287-311P (1936).

³⁴ Mayers, M. A., and Landau, H. G., Paper presented at the February 1941 meeting of the *American Institute of Mining and Metallurgical Engineers*, New York, N. Y.

ing of small-sized coke with economy. As might be expected from this fact, little attention has been paid to the physical properties of coke for such purposes; provided that it contained enough combustible matter so that its cost per million Btu was low, the coke was expected to make little or no contribution to its ease of utilization. Thus, the attention of engineers was devoted, not to the development of desirable properties of the fuel, but to the development of equipment that could handle it, regardless of its characteristics. Since, in general, such fuel resulted from the screening out of the small sizes from coke prepared for metallurgical use, equipment has been developed that is capable of handling material from 1 inch down to dust;³⁵ but sometimes,³⁶ in order to secure the increased gas production attainable with sized coke, a portion of the fine breeze (through 12-millimeter screen) has been removed from the feed to the gas producers and supplied to chain-grate stokers for steam raising. These stokers appear to be quite flexible enough to cope with any probable variations in the quality of coke without difficulty, provided that they are not forced to excessive ratings, and they are the usual devices specified for the large-scale combustion of coke breeze. A small underfeed stoker has been developed for domestic heating with coke and has been subjected to tests by a large coke producer in this country. It is likely that such a stoker would use a screened coke prepared especially for the purpose, rather than unprepared breeze. It also seems likely that coke breeze could be utilized as pulverized fuel, with equipment similar to that developed for burning an-

thracite,³⁷ but the writer knows of no instance in which this has been done.

It appears, however, that the size and size distribution of the coke are of great importance in determining both the quality of the gas and the economy and rate of operation of gas producers. Thus, Qvafoort³⁸ quoted tests of an A.V.G. producer, 2.6 meters in diameter, which, when fired with small coke, 6 to 15 millimeters in size, plus 42.8 percent of breeze 63 percent of which was smaller than 3 millimeters, burned 13.1 tons (metric) per day, producing a gas of 1,028 kilocalories per cubic meter (115 Btu per cubic foot) heating value, at a gas efficiency of 69.8 percent; the same producer, when fired with a 15 to 25 millimeter coke, with 32.4 percent of the same breeze, burned 16.8 tons of coke per day, producing a gas of 1,069 kilocalories per cubic meter (120 Btu per cubic foot) at a gas efficiency of 70.4 percent. The data available, however, are not complete enough to justify extensive analysis.

Three developments have caused much more attention to be paid to the properties of coke that is to be used as fuel for gas producers or for heating: (1) the Fischer-Tropsch process for the synthesis of liquid fuel, with its requirements of large volumes of water gas of high hydrogen content; (2) producer-gas-fired motor vehicles with their demand for large capacity in a small space; and (3) the increasing demand for solid smokeless fuel for domestic heating, especially, as in England, where the fuel is to be used in open grates. Jäppelt and Steinmann³⁸ have shown that the high hydrogen to carbon monoxide ratios required for synthesis gas can be reached in generators of

³⁵ Holton, A. L., and Applebee, H. C., *Gas J.*, **192**, 151-8 (1930). Winkler, F., and Linckh, Ed., U. S. Pat. 2,111,579 (1938).

³⁶ Qvafoort, S., *Schweiz. Ver. Gas- u. Wasserfack.*, *Monats Bull.*, **19**, 157-62 (1939).

³⁷ Frisch, M., *Trans. Am. Soc. Mech. Engrs.*, **58**, 177-83 (1936). Mayer, J., *J. Inst. Fuel*, **11**, 305-26 (1938). Johnson, E. B., *ibid.*, **12**, 177-87 (1939).

³⁸ Jäppelt, A., and Steinmann, A., *Brennstoff-Chem.*, **18**, 135-40 (1937).

commercial types, provided that highly reactive cokes are used. Though there may be some question concerning the comparisons made by these authors among fuels of various types,³⁹ their conclusion that high reactivity is essential for the practical production of synthesis gas is supported by the extensive work on a laboratory scale reported from Germany on methods of increasing the reactivity of coke and of catalyzing the water-gas reaction. (See Chapter 39.)

The development of the automotive suction gas producer in Germany and England, in those nations' search for freedom from dependence on imported oil, led to a demand for this application for a coke that is closely sized and highly reactive but which must be free of any trace of distillable tar.⁴⁰ Close sizing is necessary for two reasons: first, because the pressure drop through the producer must be kept to a minimum so that the volumetric efficiency of the engine may not be adversely affected;⁴¹ and second, so that dust carry-over by the gas, which has been the greatest source of mechanical difficulties in this application, may be minimized.⁴² Whereas Gumz claimed that physical factors—size, size distribution, void volume, etc.—are more important than chemical factors in characterizing coke to be used in gas production,⁴³ other writers have been nearly unanimous in the statement that high reactivity of the fuel is essential. In some types of producers,⁴² in order to keep the gasification rate and the quality of the gas approximately constant throughout the time

required to burn out a filling, the gas is allowed to pass through only about a quarter of the height of the coke column, the remainder of the combustion chamber serving more as storage space than as reaction space. This materially restricts the extent of the coke surface to which the reacting gases may be exposed in such producers, and a high reactivity is required to make up for the restriction.

Wohlschläger⁴⁰ and Lessnig⁴⁴ both recommended low-temperature coke made from brown coal as a suitable fuel for automotive gas producers because of its high reactivity, and a report of Sir Harold Hartley's Committee on the Emergency Conversion of Motor Vehicles to Producer Gas,⁴⁵ naming reactivity as a prime requisite of fuels for such applications, in its provisional specification, included only anthracites (uncarbonized) and low-temperature coke. The specification referred to set limits on the "potential tar" that may be distilled from the fuel as less than 15 ounces per ton of anthracite, and less than 10 ounces per ton of low-temperature coke, and specified that either fuel must be sized to remain on a $\frac{3}{16}$ -inch screen and to pass a $\frac{3}{4}$ -inch screen. This specification is reproduced in Table III. (See also Chapter 37.)

Extensive agitation for the abatement of smoke and the active and enlightened search for new and profitable markets for their coke on the part of British gas companies have led to productive research on the adaptation of coke to the open grate fire and to the development of special grates for its use. New and improved grates and fireplaces both for coke and coal have been devised,⁴⁶ and the Fuel Research

³⁹ Mücke, M., *Gas- u. Wasserfach*, **80**, 135-40 (1937).

⁴⁰ Wohlschläger, H., *Z. Ver. deut. Ing.*, **81**, 1299-304 (1937).

⁴¹ Lang, K., *ibid.*, **83**, 472-3 (1939).

⁴² Rammeler, E., Breitling, K., and Gall, J., *Feuerungstech.*, **27**, 99-102 (1939).

⁴³ Gumz, W., *Feuerungstech.*, **27**, 97-9 (1939).

⁴⁴ Lessnig, R., *Glückauf*, **73**, 1053-9 (1937).

⁴⁵ Anon., *Gas J.*, **229**, 852-3 (1940).

⁴⁶ Blackie, A., *J. Inst. Fuel*, **10**, 131-2 (1937).
Rosin, P. O., *ibid.*, **12**, 198-223 (1939).

TABLE III

PROVISIONAL SPECIFICATION OF FUELS FOR THE EMERGENCY PRODUCER⁴⁵

	Anthracite	Low-Temperature Coke
Volatile matter	Less than 7 percent	Variable *
"Potential tar"	Less than 15 ounces per ton	Less than 10 ounces per ton †
Hydrogen (dry ash- free basis)	Less than 3.7 percent
Ash	Less than 4 percent	Less than 5 percent
Moisture	Not limited ‡	Not limited ‡
Size	¾ inch by ⅜ inch	¾ inch by ⅜ inch

Volatile matter and ash determined by the methods given in British Standard Specification 735, hydrogen by the method given in British Standard Specification 687, and "potential tar" by the method described in the report.

* Should be as high as possible, provided that the limit for "potential tar" is not exceeded.

† Provisional figure.

‡ Except for fabric filters.

Board maintains a special building for research in this field.⁴⁷ Parallel with this development there has been intensive investigation of the characteristics required of coke to permit it to meet the competition of coal as a fireplace fuel and of methods of satisfying those requirements with the least possible change in the carbonizing equipment, whose primary function is the production of illuminating gas. The problems to be overcome have been: (1) to secure ease of ignition and adequate ability of the fire to maintain itself; (2) to obtain adequate radiation intensity and pleasing appearance of the fire; and (3) to overcome the disadvantage in storage and grate volume required by coke of low density. A coke with the optimum qualities from one point of view will have poor characteristics from another; that is, the optima are mutually incompatible, so that a certain degree of compromise is unavoidable. For example, a coke of low bulk density is de-

sirable to obtain ease of ignition⁴⁸ since the time required to reach a "bright fire" increases 5 minutes with an increase of 1 pound in the weight per cubic foot of the 1½-inch by 2-inch coke.⁴⁹ On the other hand, light coke will burn out rapidly since grates are filled to a fixed volume, not to a fixed weight, and will require frequent replenishment; also the storage space required to keep an adequate supply at hand may become burdensome. Another means of securing easy ignition is by using a highly reactive fuel, produced either by carbonization at low temperature or by the addition of a catalyst, such as soda or lime and soda, either to the coke or to the coal before carbonization, but this results in a lowering of the radiating power of the fire, since the increased reactivity increases the rate of gasification to carbon monoxide, increasing the proportion of the burning that takes place in the gas phase and lowering the temperature of the solid surfaces which supply the greater part of the radiation.

The problem has been attacked partly by the development of special laboratory tests, notably the C.A.B., or Critical Air Blast, Test, which is very widely used in England and is described later in this report under the heading "Tests of Reactivity," but mostly by actual test of various fuels in grates and fireplaces under more or less carefully controlled conditions. The work has resulted in fairly definite standards to which an open-fire coke should conform, which are stated below. This statement is, largely, a digest of published reports by Mott, Davidson, Cobb, and the South Metropolitan Gas Company.^{50, 51, 52} Coke for open fires should:

⁴⁸ Cobb, J. W., and Hodsman, H. J., *ibid.*, **10**, 127-9 (1937).

⁴⁹ Mott, R. A., *ibid.*, **10**, 133-5 (1937).

⁴⁷ Blackie, A., and Bruckshaw, J. M., *ibid.*, **12**, 20-7 (1938).

⁵⁰ Anon., *Gas J.*, **202**, 162-3 (1933.) Stubbs, A. E., *J. Inst. Fuel*, **10**, 125-48 (1937). Brewin,

1. Be closely sized, all passing a 2-inch screen and remaining on a 1-inch screen, perhaps 80 percent being smaller than $1\frac{1}{2}$ inches.

2. Have a bulk density, as fired, in the neighborhood of 19 to 22 pounds per cubic foot.

3. Be fairly reactive, having a C.A.B. value below 0.06, and preferably in the neighborhood of 0.04. More reactive cokes can be burned satisfactorily in larger sizes, making a somewhat pleasanter fire to the eye; or the bulk density of such coke may be higher.

4. Have low ash volume, though not necessarily low ash content by weight. The ash should fall away from the coke in fairly large pieces. Thus, it is usually undesirable to make open-grate coke from finely crushed blends of coal; in fact, Davidson⁵² recommended the coking of 3-inch nut coal.

5. Have low, accurately controlled moisture content, in the neighborhood of 3 percent, to minimize the possibility of dust nuisance on delivery, but low enough so that there will be little danger of decrepitation of shale particles during burning.

Many methods for securing this combination of properties using either gas retorts or coke ovens have been developed. Some of them have been mentioned above; others will be treated in later sections of this report in connection with methods of influencing the properties of coke. Brewin and Mott⁵⁰ listed seven different methods of making coke of high reactivity in coke ovens.

For use in stoves and central heating boilers, the requirements of a satisfactory

coke are somewhat less stringent. The reactivity of the coke may be somewhat lower, i.e., it may have a higher C.A.B., for most purposes, but for small hot-water boilers in use abroad, in which a low load is carried almost all the time, as low a C.A.B. value is necessary as for open fires. The coke should usually be smaller, but a double-screened coke is considered necessary, the sizes recommended being $\frac{3}{8}$ by $\frac{5}{8}$ inch and $\frac{5}{8}$ by 1 inch,⁵³ or $\frac{5}{8}$ by $1\frac{1}{4}$ inches.⁵⁴ For hot-water heating and central heating unit firing, high bulk density is a distinct advantage as it reduces the attention required.^{51, 52}

For chain-grate stokers, the reactivity of the coke helps to determine the maximum rating that may be carried because of its influence on the rate of ignition in pure underfeed burning, which, as shown in Chapter 33, is similar to the process occurring in the fuel beds of these stokers. The effects of some of the other properties of coke on its reactions in this equipment can be estimated from the conclusions reached in later sections of this report (pp. 901 and 912), but exact information on the effect of coke size and size distribution on maximum capacity and average operating efficiency is not available.

It will be observed that the requirements for coke for these purposes are generally more definitely known than those for blast-furnace cokes. This is because, since the units are usually small, it is possible accurately to control the conditions of their operation for long enough to secure test measurements of reasonable precision. On the other hand, the factors governing the suitability of cokes (and of coals, too, for that matter) for large power boilers are not entirely understood. For this use, also, corre-

W., and Mott, R. A., *Gas World*, **110**, Coking Sect., 55-60 (1939).

⁵¹ South Metropolitan Gas Company, *The Solid Products of Carbonization of Coal*, So. Met. Gas Co., London, 1934, pp. 62-104.

⁵² Davidson, W., *Gas J.*, **218**, 211-4, 280-8 (1937).

⁵³ See pp. 110-1 of ref. 51.

⁵⁴ Eaton, F. J., *Gas J.*, **222**, 562-70, 808-16, 976-8 (1938).

lation of operating records with fuel properties over long periods of time is probably necessary. Data for an example of this are not available.

TESTS OF COKE PROPERTIES

STRUCTURAL PROPERTIES

The term structural properties of coke is used here to classify all those properties of the coke which help to determine the structure of the bed it forms when piled, as in a fuel bed or a blast-furnace stock column. The structure of this bed determines the resistance to gas flow through it, which, as has been noted, is a property of fundamental importance in every application. Carman⁵⁵ has shown that the resistance of a bed to the passage of a fluid depends on two characteristics: the volume of voids, and the specific surface, i.e., the area exposed to fluid friction per unit volume of the bed. Both these quantities may be measured directly, under some circumstances, but they may also be estimated from a knowledge of the size and size distribution of the coke as it is charged, if some information is available about the degree of packing that is achieved in the charging process. Differences in size are obvious to the eye, so that differences in behavior ascribable to changes in the void volume or specific surface are usually attributed to changes in the size. Thus, the measurement of the size of coke has become very important.

It must be noted, however, that the values of these fundamental variables which are significant for practice are those in the bed formed in the equipment in which the coke is used. It usually happens that the size or the bulk density of the coke is measured at the point at which the coke is pro-

duced, after which the coke is handled more or less severely in shipment to the point of use. When this occurs, or when the coke may be degraded in the process in which it is used, as in passing down through the shaft of a blast furnace, the size, size distribution, void volume, and specific surface may change materially from the point of measurement to the point of use. Thus, in order to estimate the properties of the bed it may be necessary to form an estimate of the extent to which the coke has been degraded by handling, either in shipment or in the process itself. These facts indicate why strength tests of coke have assumed such great importance; since they measure properties which influence the structure of the bed as charged, they are included here under the heading of structural properties.

Finally, since the void volume of the bed is of primary importance, the determination of bulk density and of apparent specific gravity, from which it may be calculated, is included in this section. The determination of true specific gravity is also included because it is usually carried out at the same time as the determination of apparent specific gravity, although there is little evidence that it has any significance except as an indicator of the degree of graphitization of the coke, a subject treated in a later section.

Size and Size Distribution. The determination of coke size is important, not only in itself, but also because it forms an integral part of almost all the tests of coke strength, whose results are usually reported in terms of the size of coke resulting from some standardized treatment of a sample of known initial size. It is obtained by screening a sample of coke on a series of sieves of standard dimensions, the results being reported, alternatively, as the percentages by weight of the sample between each pair remaining on the largest and passing through

⁵⁵ Carman, P. C., *Trans. Inst. Chem. Engrs. (London)*, **15**, 150-86 (1937).

the smallest, or as the cumulative percentage on each sieve. A standard method for the determination has been set up by the American Society for Testing Materials,⁵⁶ which specifies in detail the procedure to be followed in carrying out such tests and the dimensions of the sieves to be used.

The American standards for the tumbler and shatter tests, for both coal and coke, also contain specifications of the sieves to be used in reporting the results of the tests. In the tumbler test, the sieves are part of the same series as those for tests of coke size, namely, the square-mesh sieves continuing the Standard Fine Series⁵⁷ omitting every other one, so that the ratio between the apertures of successive sieves is $\sqrt{2}$ (1.414). Instead of even dimensions at $\frac{1}{4}$, $\frac{1}{2}$, and 1 inch, the sieves for this series have openings of 0.263, 0.525, and 1.050 inches. For the shatter test, however, the specification requires the use of the even-dimension screens at $\frac{1}{2}$ and 1 inch. If the screens specified for sizing coal are considered, the situation becomes even more confused. For crushed bituminous coal to be charged to coke ovens, the standard⁵⁸ specifies the same screens as are used for sizing coke, but for coal (except anthracite) for all other purposes, the standard⁵⁹ requires round-hole punched-plate sieves for all sizes larger than the Fine Series, starting with $\frac{3}{8}$ -inch diameter. No advantage appears to be gained by this diversity of sizes, and it seems desirable that it be eliminated.

The British Standards Institution has set up a specification⁶⁰ for sieves of three

series: Fine, Medium, and Coarse Mesh, all having square apertures, and the Coarse Series, with punched-plate screens. Screens from these series are specified for all British tests of coal and coke,⁶¹ so that the confusion existing in American practice does not occur. Evidently punched-plate screens have a decided advantage for large apertures in durability and in maintenance of accuracy of opening, but there seems to be no good reason, except, perhaps, established usage, for using round-hole sieves and square-mesh screens in the same series. The relative sizes of particles passing square-hole and round-hole screens of the same size designation is open to some question; it is evident that for very thin plates the ratio of the diameters would be 1.414. Heywood⁶² found the average "equivalent" diameters of coal particles passing square and round-hole sieves to be equal to 1.41 times the opening of a square mesh, and 1.21 times the opening of a round-hole screen, giving a ratio of 1.16. In this country the factor frequently used for conversion is 1.25. Though the difference between the last two factors is not great, it would be desirable to eliminate the need for inter-conversion by using only square openings.

Although the odd-sized screens mentioned above, 0.263, 0.525, and 1.050 inches, are used to continue a rational series, their value does not appear great enough to justify the possibility of their confusion with $\frac{1}{4}$ -, $\frac{1}{2}$ -, and 1-inch screens. Furthermore, if the methods of correlating screen analyses described below, which permit the complete description of most analyses by only two parameters, become general, there will no longer be any advantage in the use of screens whose openings differ by *exactly* $\sqrt{2}$; in fact, screens of simple dimensions

⁵⁶ Am. Soc. Testing Materials Standard D293-29.

⁵⁷ Am. Soc. Testing Materials Tentative Standard E11-38T.

⁵⁸ Am. Soc. Testing Materials Standard D311-30.

⁵⁹ Am. Soc. Testing Materials Standard D410-38.

⁶⁰ Brit. Standard Specification 410-1931.

⁶¹ Brit. Standard Specification 496-1933.

⁶² Heywood, H., *Proc. Inst. Mech. Engrs. (London)*, **125**, 383-459 (1933).

would be more advantageous because of the increased facility of plotting on, rather than between, ordinates.

In the late '30's work on sizing was more directly applied to the sizing of coal, being especially concerned with sampling methods and with the concise representation of the results of sieve analyses. Statistical theory has been very fruitful in this field, and, though it has been applied more frequently to the requirements of sampling for the elimination of errors in the estimation of the chemical analysis,⁶³ the field of sampling for size analysis has not been neglected.⁶⁴ The fundamental basis for the estimation of the sizes of gross samples required for these analyses is that, as the number of increments by which the gross sample is taken is increased, the average value of any analytical property determined from the sample approaches the mean value of that property for the entire consignment and is normally distributed about that mean; that is, its distribution about the true mean may be calculated from the normal or Gaussian error function, with a standard deviation equal to:

$$\sigma_m = \frac{\sigma}{\sqrt{N}} \quad (1)$$

where σ_m is the standard deviation of the mean of the property, or of the value obtained by the analysis of a sample taken by N increments, when the standard deviation for a single increment is given by σ . That this law holds has been demonstrated experimentally for the ash content of coal^{65, 65, 66} and for the moisture content

of coke,⁶⁷ so that it may confidently be expected to hold for the size analysis of coke as well. The quantity σ depends on the variability of the consignment and the size of the increments taken, and thus may be quite different for increments of a given size, depending on whether the sample is to be used for size analysis or for chemical analysis.

The standard method of sampling coke for chemical analysis⁶⁸ specifies the gross sample sizes given below:

	POUNDS
Run-of-oven, etc., coke containing a range of sizes made from uncrushed or coarsely crushed coal	500
Run-of-oven, etc., coke made from crushed coal	250
Closely sized coke made from uncrushed or coarsely crushed coal	250
Closely sized coke made from crushed coal	125
Coke breeze	125

Although these evidently were not determined by as rigorous application of statistical theory as those given in the method for sampling coal classified as to ash content,⁶⁹ they are not very unlike those given there if coke from uncrushed coal is considered to have a variability equivalent to that of coal of greater than 10 percent ash content, whereas that from crushed coal has a variability equivalent to that of coal having 8.0 to 9.9 percent ash. Comparing the gross sample sizes of coal specified for chemical⁶⁹ and size⁵⁰ analyses, it will be observed that the size analysis calls for samples from 2½

ards Specifications 403 (1930) and 502 (1933).

⁶⁶ Dawe, A., and Potter, N. M., *Fuel*, **15**, 128-36 (1936).

⁶⁷ Mott, R. A., and Wheeler, R. V., *The Quality of Coke*, Chapman and Hall, London, 1939, pp. 42-69.

⁶⁸ Am. Soc. Testing Materials Standard D346-35.

⁶⁹ Am. Soc. Testing Materials Tentative Standard D492-38T.

⁶³ Morrow, J. B., and Proctor, C. P., *Fuel*, **16**, 128-47 (1937). Bushell, L. A., *J. Chem. Met. Mining Soc. S. Africa*, **37**, 361-434 (1937); cf. *J. Inst. Fuel*, **10**, 384-408, **11**, 50-67 (1937).

⁶⁴ Manning, A. B., *J. Inst. Fuel*, **11**, 153-5 (1937).

⁶⁵ Grumell, E. S., and Dunningham, A. C., *Fuel*, **15**, 55-9 (1936). Cf. also British Stand-

times for small coal, to 10 times for large coal, as large as those required for chemical analysis. On this basis, the minimum gross sample sizes of coke that might be expected to give results of precision equivalent to that of chemical analysis might be of the order of the following:

	POUNDS
Run-of-oven coke, top size 4 inches or larger	5,000
Run-of-oven coke, top size 2 to 4 inches	2,000
Closely sized coke, top size 4 inches or larger	2,000
Closely sized coke, top size 2 to 4 inches	1,000
Coke, top size 1 to 2 inches	500
Coke breeze (smaller than $\frac{3}{4}$ inch)	250

The standard specification,⁵⁶ however, calls for gross sample sizes as follows:

	POUNDS
Run-of-oven coke 1 inch and larger	Not less than 500
Coke 1 inch and larger, free from breeze	Not less than 200
Coke smaller than 1 inch in size	Not less than 50

This specification appears to be inadequate, especially in view of the fact that the minimum number of increments to be taken and the size of the increments are not stated. On the other hand, the estimate given above, based on the comparison of the coal standards for chemical and size analyses, appears to be unnecessarily burdensome in the light of the results of Clive and Slater's coal-sampling tests,⁷⁰ reproduced in Table IV, and of Manning's calculations of the deviations to be expected, given in Table V. Extending these results to the range of sizes found in large coke, where one piece might weigh 4 pounds, it would be necessary, in order to secure precision equivalent to that of the 150-pound gross samples of Table

⁷⁰ Clive, R., and Slater, L., *Trans. Inst. Mining Engrs. (London)*, **94**, 41-69 (1938).

TABLE IV

SIZE ANALYSIS OF 50 TONS OF TREBLES FROM 21 GROSS SAMPLES EACH COLLECTED IN TWENTY-FIVE 5-POUND INCREMENTS ⁷⁰

Weight of gross sample, pounds	Mean	Deviations	
	130	Standard	19/20 Chance *
Screen analysis, percent			
On $2\frac{1}{4}$ -inch square	4.6	1.19	2.33
On $1\frac{3}{4}$ -inch square, passing $2\frac{1}{4}$ -inch	36.3	2.28	4.46
On $1\frac{1}{4}$ -inch square, passing $1\frac{3}{4}$ -inch	52.9	1.91	3.74
On $\frac{3}{4}$ -inch square, passing $1\frac{1}{4}$ -inch	5.6	0.73	1.43

* Deviation from the mean within which 95 percent of the results may be expected to fall.

TABLE V

THEORETICAL DEVIATIONS OF SIZE ANALYSES ACCORDING TO MANNING ⁷⁰

Colliery Size	Weight of Largest Particle pounds	Weight of Gross Sample pounds	Precision of Screening *		
			5 or 95%	10 or 90%	50%
3 to 2 inches	0.5	100	3.0	4.2	6.9
		500	1.4	1.9	3.1
		1,000	1.0	1.3	2.2
		2,000	0.7	0.9	1.6
2 to 1 inch	0.2	100	1.9	2.6	4.4
		300	1.1	1.5	2.5
		500	0.9	1.2	2.0
		1,000	0.6	0.8	1.4
1 to $\frac{1}{2}$ inch	0.05	50	1.4	1.9	3.1
		100	1.0	1.3	2.2
		150	0.8	1.1	1.8
		200	0.7	0.9	1.6

* Deviation from mean within which 95 percent of the results may be expected to fall, when the mean (percent retained on, or passing) has the magnitude indicated by the column heading.

IV, to take 1,000-pound gross samples in 25 increments of 40 pounds each, instead of the 5,000 pounds estimated above. It is desirable that additional work be done in this field so that gross sample sizes can be correctly chosen for various standards of precision of size analysis.

PHYSICAL PROPERTIES AND REACTIVITY OF COKE

Concise representation of size analyses of broken solids is made possible by the fact that many such distributions can be represented by continuous functions which are completely specified by a small number of, usually two, parameters. The first of these functions to be applied successfully to coal was developed by Rosin and Rammler⁷¹ and is usually referred to by their names. The Rosin-Rammler law states that the size of powdered coal is distributed in accordance with the expression:

$$R = 100e^{-bx^n} \quad (2)$$

where R represents the percentage by weight retained on a sieve of opening x , and b and n are arbitrary constants, to be determined for any particular sample, which completely specify the distribution of that sample. By twice taking logarithms of both sides this becomes:

$$\log \log \frac{100}{R} = \log b + n \log x \quad (3)$$

so that a linear plot of the results of sieve analyses can be made on paper having coordinates $\log \log 100/R$ and $\log x$. The slope of the line on such a graph is the parameter n , and the value of x at which the line crosses the coordinate corresponding to $R = 36.8$ percent is equal to $1/b$. The latter parameter is related to the average size of the distribution; the former represents the closeness of the sizing; the greater n is, the closer is the bulk of the coal to the average size, and vice versa. It has been shown⁷² that the same distribution law applies to broken coal of large sizes, provided that the distribution has not been disturbed by screening or recombining, and that the law applies as well to

American coals.⁷³ Yancey and Geer have also given tables of values of $\log \log 100/R$ by whose use ordinary semilogarithmic paper can be converted to coordinates suitable for plotting the Rosin-Rammler law.

Another method of representing screen analyses, which from some points of view is to be preferred to the Rosin-Rammler law, has been suggested by Austin,⁷⁴ in which the percent by weight remaining on a sieve is plotted on probability coordinates against the sieve opening. The reasons for preferring this representation to the Rosin-Rammler law are: first, that the specific surfaces may, under some conditions, be more easily calculated from this distribution; and second, that paper printed with the proper coordinates is available from stationery supply houses. It is found that with some materials straight lines on these coordinates are obtained when the size scale is logarithmic; this is true for broken coal. On the other hand, for the large coke produced in coke ovens, straight lines are found when paper having regular or arithmetic scales for size is used, as shown in Fig. 1A. It will be observed that the straight line represents the distribution down to the smallest 5 percent but that the distribution often falls much below the line for the very finest materials. On the other hand, the small sizes produce a straight line when plotted to logarithmic size coordinates as shown in Fig. 1B. This anomaly is related to the facts that the size distribution of coke degraded by shattering is very accurately represented by a straight line using arithmetic size coordinates, whereas the size of coke degraded by abrasion, as the small coke formed in the tumbler test, is not. Since the samples rep-

⁷¹ Rosin, P., and Rammler, E., *J. Inst. Fuel*, **7**, 29-36 (1933).

⁷² Bennett, J. G., *J. Inst. Fuel*, **10**, 22-39 (1936).

⁷³ Geer, M. R., and Yancey, H. F., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 250-69 (1938).

⁷⁴ Austin, J. B., *Ind. Eng. Chem., Anal. Ed.*, **11**, 334-9 (1939).

resented in Fig. 1 are the entire product discharged from the ovens, without the removal of breeze, the departure from the line indicates that a proportion of the coke is degraded by abrasion in pushing and handling on the wharf.

Referring now to Fig. 1A, the ordinate of the curve at the center of the horizontal scale, that is, the value at 50 percent on, is the average size and is one of the parameters which represents the size distribution. The other parameter, which measures the closeness of the sizing, may be chosen in several ways, but perhaps the most con-

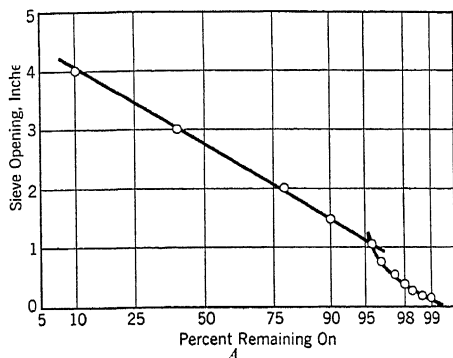


FIG. 1. Coke-size distribution to probability coordinates.

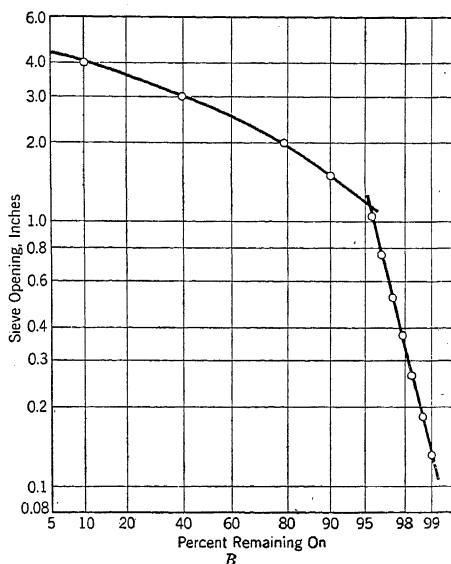
A. With arithmetic size coordinates. Characteristics of straight line $M = 2.77$ inches, $S = 0.67$ inch.

B. With logarithmic size coordinates, showing that curved portion of A becomes straight line in B.

$$R = 50 \mp 50 \operatorname{erf} \left\{ \pm \frac{(x - M)}{1.047S} \right\} \quad (4)$$

where erf represents the ordinary error function

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (5)$$



venient one is the value of the "quartile deviation," the distance on the ordinate from the point at which the line crosses the 50 percent abscissa to that at which it crosses the 75 percent line. This parameter is analogous to the "probable error" of an observation, in that 50 percent of the weight of the coke falls between the limits of $M + S$ and $M - S$, where M represents the mean size and S represents the quartile deviation, referred to in the Coal Research Laboratory as the "spread."

This representation of coke size lends itself easily to calculation. In the first place, the size distribution is represented by:

and R is the percent by weight remaining on a screen of opening x .

Specific Surface. The specific surface of a granular material may be stated either as the exposed surface in a unit of volume of the bed, when it is dependent not only on the sizing of the material as charged but also on the density of packing, or, more conveniently, as the surface exposed per unit of weight of the material. The latter practice is more common with respect to coke. As noted above, the specific surface may be calculated from the size analysis, provided that certain shape factors are known. These shape factors, which have

been determined for coal by Heywood⁶² and for coke by Gabinskii and Badanova,⁷⁵ are defined as:

$$k = \frac{V}{d_e^3} \quad (6)$$

where k is the volume shape factor, V is the average particle volume of a given size fraction, and d_e is the equivalent diameter of the size fraction,⁶² and:

$$f = \frac{S}{d^2} \quad (7)$$

where f is the surface shape factor and S is the average particle surface of a given size fraction.

Using this notation and natural logarithms, the specific surface of a sample whose analysis satisfies a straight line on logarithmic-probability coordinates is given by:

$$\log S = \log \frac{f}{\rho k} - \log M + \frac{1}{2} \log^2 \sigma_g \quad (8)$$

where ρ is the apparent density of the coke and M and σ_g are the logarithmic mean size by weight and the logarithmic standard deviation, respectively, the latter being given by the ratio:

$$\sigma_g = \frac{\text{Size at 84.13 percent}}{\text{Size at 50.00 percent}} \quad (9)$$

Moreover, the fraction of the total surface or of the specific surface between any two limits within the range covered by the distribution law can be calculated from the formula:

$$S_{a-b} = \frac{\operatorname{erf} \left[\frac{\log b - \log M + \log^2 \sigma_g}{\sqrt{2} \log \sigma_g} \right] - \operatorname{erf} \left[\frac{\log a - \log M + \log^2 \sigma_g}{\sqrt{2} \log \sigma_g} \right]}{\operatorname{erf} \left[\frac{\log b - \log M}{\sqrt{2} \log \sigma_g} \right] - \operatorname{erf} \left[\frac{\log a - \log M}{\sqrt{2} \log \sigma_g} \right]} \quad (10)$$

where S_{a-b} represents the specific surface between the size limits a and b and S repre-

sents the specific surface of the entire sample given by equation 8.

These calculations cannot be so easily made when the size distribution is represented by a line on arithmetic probability paper. They can, however, be performed arithmetically by the solution of the cubic equation given by Austin⁷⁴ for D , which is equivalent to the quantity M used here.

In addition to these indirect methods of determining specific surface by calculation from the size analysis, Carman⁷⁶ has shown that the specific surface of fine powders may be measured directly by determining the resistance to flow through a bed of known void volume of a fluid flowing in the viscous regime. Under these conditions, the specific surface, in terms of the actual volume of solids in the powder, is given by:

$$S_0 = 14 \sqrt{\frac{1}{K\nu} \frac{\epsilon^3}{(1-\epsilon)^2}} \quad (11)$$

where S_0 is the specific surface per unit volume of powder, ϵ is the volume of voids in the bed, ν is the kinematic viscosity of the fluid used in the determination, and K is the hydraulic gradient, or loss of pressure per unit length of flow path, per unit velocity. The specific surface per unit weight is obtained by dividing by the apparent density of the material. The papers referred to are devoted to showing that the equation does hold for a large number of powders whose surfaces could be calculated from microscopic analysis and for mixtures

of powders of different particle sizes, each of whose surfaces was determined by this

⁷⁵ Gabinskii, Y. O., and Badanova, S. I., *Fuel*, **16**, 85-92 (1937).

⁷⁶ Carman, P. C., *J. Soc. Chem. Ind.*, **57**, 225-34T (1938), **58**, 1-7T (1939).

method. The method has been applied by Lea and Nurse⁷⁷ with a simplified apparatus, illustrated in Fig. 2, and with air as the measuring fluid. They showed that, if

$$\rho(1 - \epsilon) \sqrt{\frac{\epsilon^3 A h_1}{C L h_2}} \quad (12)$$

where ρ is the apparent density of the material, A is the cross-sectional area of the bed of powder, L its depth, h_1 and h_2 the readings of the pressure drop and flowmeter manometers, respectively, and C the flowmeter coefficient defined by:

$$Q = C \frac{h_2 \rho_4}{\mu} \quad (13)$$

where ρ_4 is the density of the manometer fluid, μ is the absolute viscosity of the air, and Q is the rate of air flow through the manometer. The measurements of specific surface were found to be independent of the diameter of the measuring cylinder for cement powders, and independent of air-flow rate in the neighborhood of rates of flow given by:

$$Q = 1.5 \times 10^{-4} \quad (14)$$

The method has not been used for the measurement of the specific surface of beds of large particles, but it probably could be if the container in which the measurements are made is large enough in cross section to eliminate wall effects. It may, however, be more convenient to calculate the specific surface of large pieces, for which the experimental determination of shape factors is reasonably easy,⁷⁸ and to reserve this method for surface measurements on powders for which the determination of shape factors verges on the impossible.

Coke Strength. The most common measurements of coke strength are its resistance to shatter in the standard American test and its resistance to degradation by tumbling as in the American tumbler or in the Cochrane test or in the "Micum" tumbler.

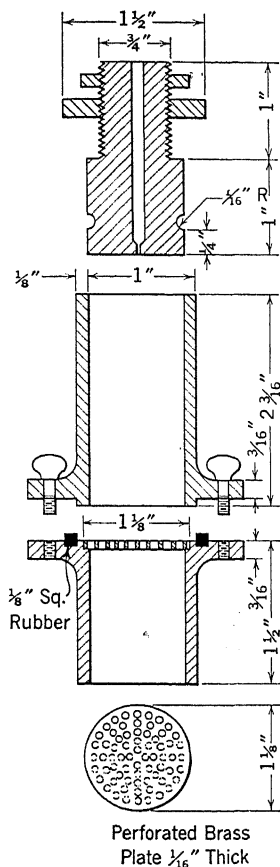


FIG. 2. Apparatus for determination of specific surface of powders by Carman's method according to Lea and Nurse.⁷⁷

the pressure drop through the manometer used for the measurements of flow rate and that through the powder are measured by the same liquid, the specific surface per unit mass, S_w , is

⁷⁷ Lea, F. M., and Nurse, R. W., *ibid.*, 58, 277-83T (1939).

⁷⁸ Needham, L. W., and Hill, N. W., *Fuel*, 14, 222-30 (1935).

In addition to these, there are a number of other tests of coke strength, some of them merely modifications of the standard tests devised for study of smaller samples than can be used in the standard ones or dictated by the experimenter's personal preferences, and others altogether different in principle. The modifications will be described with the standard test to which they approximate; the others, in a later paragraph.

(a) Shatter Test. The American standard shatter test⁷⁹ is so well known that only a brief description is necessary. Fifty pounds of coke, all over 2 inches in size, is dropped four times from a height of 6 feet on a steel plate, and the resulting degraded product is sieved on 2-, 1½-, 1-, and ½-inch screens. The shatter index is frequently reported as the percentage by weight remaining on the 2-inch screen, but reporting the complete size analysis is a practice much to be preferred and is, in fact, specified in the standard. The coke is dropped from a box 18 inches wide, 28 inches long, and about 15 inches deep, having doors on the bottom, hinged lengthwise and latched so they swing open freely and do not impede the fall of the coke. The box is usually supported by counterweighted cables, although other arrangements have been suggested,²⁸ so that it may be lowered for convenience in shoveling the broken coke back into it between drops.

The British standard test⁸¹ is essentially the same as the American except for the more rigorous specification of the method of sampling coke for the test, and of the number of tests to be made and their agreement. In both respects the British test is

probably an improvement on the American one. Whereas the American standard specifies that 75 pounds of full-length pieces shall be taken as a gross sample, the British specification calls for 250 pounds of pieces larger than 2 inches, collected by increments of single pieces distributed evenly over the whole consignment, and representative of the sizes of the lumps in the consignment. It is hard to believe that a gross sample of 75 pounds of full-length pieces can be even approximately representative of a consignment of any size, and, in fact, careful workers in this country have almost invariably used much larger gross samples. Whereas the American standard recommends that several tests be made, and that the average sizing be reported, the British standard specifies that at least three tests shall be made, and further requires that "If the average deviation of the individual results from their mean exceeds 2.5 and 1.5 units with the 2- and 1½-inch screens, respectively, a further series of at least two tests shall be made and the average of all the results taken." It seems desirable that the American standard be modified to conform with this practice.

According to Briscoe and Marson,⁷⁹ the variability of the results of shatter tests, as measured by the deviation corresponding to a probability of occurrence of once in 11 times, depends on the coke and on the index taken. Thus, for 2 Durham, 1 Cumberland, and 1 Scottish cokes these deviations were 1.9, 2.2, 2.7, and 2.2 percent for the 2-inch index and 0.8, 1.1, 1.9, and 2.0 percent for the 1½-inch index, respectively. Mott and Wheeler⁸⁰ have given probable errors (about 0.4 times the 1/11 error) for the 1½-inch index ranging from 0.58 for a Durham coke to 1.35 for a Scottish one. Results obtained in the Coal Research Lab-

⁷⁹ Am. Soc. Testing Materials Standard D141-23. Kinney, S. P., and Perrott, G. St. J., *Ind. Eng. Chem.*, **14**, 926-31 (1922). Braunscholtz, W. T. K., Nave, G. M., and Briscoe, H. V. A., *Fuel*, **7**, 100-17 (1928). Briscoe, H. V. A., and Marson, C. B., *ibid.*, **10**, 464-71 (1931).

⁸⁰ See p. 121 of ref. 67.

oratory for a single blast-furnace coke of standard deviations of 1.2 percent in the 2-inch index (probable error = 0.81) are in the same range as those observed in England.

The shatter test has been criticized for not placing an upper limit on the size of pieces taken for test,⁸¹ which is probably a just criticism if the object is to measure a criterion of strength only; on the other hand, if, as seems to be frequently true, the measurement desired is a combination of a criterion of strength with an estimate of the amount of large coke that will remain after a specified amount of handling, the present specification is the proper one. It is based on the work of Kinney and Perrott⁷⁹ who found smaller deviations of the results of individual tests when full-length pieces were taken. Several of the European unstandardized shatter tests use coke sized between upper and lower limits.

Though some of the European workers use a shatter test from a 2-meter height, comparable to the American and British 6-foot drop,⁸² a greater height of drop is more common. Tobler⁸³ described a test in which 20 kilograms (44 pounds) of coke sized between 60 and 90 millimeters is dropped four times from a height of 3 meters (9.8 feet), the percentages remaining on 15-, 25-, 40-, and 60-millimeter sieves being determined after each drop. The shatter index reported in his work, however, was the percentage between 60 and 90 millimeters after four drops. An even greater difference from the standard methods is exhibited by a test⁸⁴ in which 100

kilograms (220 pounds) of coke between 40 and 60 millimeters is dropped from a fork held 3.5 meters (11.5 feet) above a cement floor, the fork being moved around so that the falling coke will land on the floor and not on other pieces of coke. It would seem difficult to standardize this test.

In order to apply a shatter test to cokes made on a small laboratory scale, Burdekin and Mott⁸⁵ described a test in which from 2 to 10 grams of coke screened on a 5-mesh sieve may be used. The coke was dropped three times inside of a vertical glass tube, 3 inches (75 millimeters) in diameter, 3 feet (0.916 meter) long, on a shallow glass dish. The "hardness" reported was the percentage by weight of the original coke remaining on a 60-mesh sieve, but as this value was found to be closely correlated with a laboratory-scale abrasion-test value, obtained by a method described below, little work has been done with the method. It seems possible that, if a larger screen were used for determining the results of the laboratory shatter test, it might be of value in comparing the cokes obtained under carefully controlled conditions in laboratory-scale carbonization experiments.

The unwieldiness of the method of reporting shatter-test results has led to considerable search for simpler ways of giving this information than the complete screen analysis. Yancey and his coworkers⁸¹ suggested the use of a single friability index, calculated from the results of the shatter test, which represents the degree of degradation of size suffered by the whole coke during treatment. Mott and Wheeler, in the First Report of the Midland Coke Research Committee,⁸⁶ laid a good deal of stress on the relation between the 2- and

⁸¹ Yancey, H. F., Zane, R. E., Fatzinger, R. W., and Key, J. A., *U. S. Bur. Mines, Tech. Paper 597* (1939), 44 pp.

⁸² Jenkner, A., Kühlwein, F. L., and Hoffmann, E., *Glückauf*, **70**, 473-81 (1934).

⁸³ Tobler, W., *Schweiz. Gas- u. Wasserfach., Monats-Bull.*, **10**, 32-8 (1939).

⁸⁴ Bunte, K., and Brückner, H., *Gas- u. Wasserfach*, **82**, 162-3 (1939).

⁸⁵ Burdekin, L., and Mott, R. A., *Fuel*, **12**, 236-9 (1933).

⁸⁶ Mott, R. A., and Wheeler, R. V., *Coke for Blast Furnaces*, The Colliery Guardian Company, London, 1930, pp. 100-7.

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the 1½-inch indexes, but in the later report⁸⁷ this emphasis has been dropped. As mentioned above, it has been found in the Coal Research Laboratory that the results

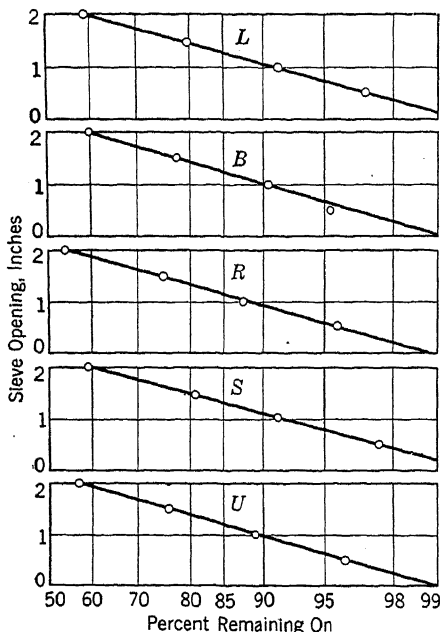


FIG. 3. Size distribution of cokes after shatter test to arithmetic probability coordinates.

Coke	Carbonization Method	Coke Temperature, °F
L	Horizontal retorts	1,910
B	Continuous vertical retorts	
R	Small intermittent vertical retorts	1,952
S	Large intermittent vertical retorts	
U	Byproduct coke ovens	1,993
All cokes made from Pittsburgh Seam coal.		

of shatter tests can almost always be represented as straight lines on arithmetic probability paper. An example is shown in Fig. 3, in which the shatter tests of five cokes made from the same coal in different types of plants⁸⁸ are plotted. The data fit the straight lines well within their precision; it

will be observed that the slope and position of the lines appear to be nearly independent of the method of coking and to be determined largely by the coal and the temperature at which it was carbonized. This result is the more remarkable in view of the facts that the carbonization equipment covers almost the whole range of commercial practice, and that, though the size distribution of the coke discharged from the ovens or retorts represented straight lines on these coordinates for every coke but that designated "B," even this coke shows the same shatter-test characteristic as the others.

The relations between the coal characteristics and the conditions of carbonization on the one hand, and the results of the shatter test on the other, will be considered at greater length in a later section. At present it may be noted that the entire shatter test is represented by the specification of the mean and the spread characterizing the line on arithmetic probability paper determined by the size analysis of the shattered coke. In conformity with the nomenclature above in connection with the specification of coke size, these two criteria will be hereafter represented by M_s and S_s , the mean and the spread of the distribution, respectively, the subscript s being used to differentiate these characteristics of the shatter test from the same characteristics of the size distribution.

(b) Tumbler Tests. Three different tumbler tests are more or less generally employed: the American standard,⁸⁹ the British standard or Cochrane,⁹⁰ and the "Mi-

⁸⁹ Am. Soc. Testing Materials Standard D294-29. Kinney, S. P., and Perrott, G. St. J., in ref. 79. Haven, W. A., *Yearbook Am. Iron Steel Inst.*, 16, 171-210 (1926). Powell, A. R., and Gould, D. W., *Ind. Eng. Chem.*, 20, 725-9 (1928).

⁹⁰ British Standard Specification 735 (1937).

⁸⁷ See pp. 115-131 of ref. 67.

⁸⁸ Anon., *Proc. Am. Gas Assoc.*, 1926, 1106-18.

cum."^{14, 91} These tests are alike in that, in each of them, a charge of coke of specified weight and particle size is placed in a horizontal cylinder of stated dimensions, which is then rotated for a specified time at a specified rate. The degraded coke is removed and sieved, the percentages on certain screens being given as results of the test. The similarities and differences among these tests are shown in Table VI. All the

to 25 percent as in other drum tests, and rotated at 23 rpm for a half hour, when the charge is screened on a $\frac{1}{2}$ -inch sieve;⁹² or, as later modified,⁹³ rotated at 60 rpm for 12½ minutes and then sieved on an $\frac{1}{8}$ -inch screen. The first modification was compared with the results of a "true" abrasion test, in which the weight loss of a sample of coke held against a grinding wheel with a known pressure was deter-

TABLE VI
SPECIFICATIONS FOR TUMBLER TESTS

	A.S.T.M.	B.S.S.	Micum
Drum			
Diameter	36 in.	30 in.	1,000 mm
Length	18 in.	18 in.	1,000 mm
Lifters, number	2	2	4
Size of angles	2 in. \times 2 in. \times $\frac{1}{4}$ in.	2½ in. \times 2½ in. \times $\frac{3}{8}$ in.*	100 mm \times 100 mm
Rotated at, rpm	24 \pm 1	18 \pm 2	25 \pm 1
for	1,400 rev.	1,000 rev.	100 rev.
Sample weight	22 lb	28 lb	50 kg
Sample sizing	2 in. sq \times 3 in. sq	2 in. sq. \times 3 in. sq	To be taken with fork with 50 mm between prongs
Sizing of degraded coke reported on	2 in., 1.5 in., 1.050 in., 0.525 in. and 0.263 in., all sq mesh	$\frac{1}{8}$ in. sq mesh	100 mm, 80 mm, 40 mm, 20 mm, 10 mm round hole

* Angles inclined 17° to horizontal plane through axis of drum.

drums are equipped with lifters so that the coke is allowed to drop freely in all of them, resulting in a certain amount of shattering action. The tests are supposed to be of particular value, however, in indicating the resistance of the coke to abrasion.

The discovery⁹¹ that the results of the Micum test actually were parallel to the shatter test led Mott and Wheeler to a search for a test that produced a more nearly true abrasive action. This led to the development of one in which a constant volume, rather than a constant weight, of coke is charged into a drum which is 75 percent filled by the charge, instead of 10.

mined, when it was found that a series of seven cokes was placed in nearly the same order in both tests, although this order differed materially from that in which the cokes were placed when the drum was filled with a constant weight of coke.⁹⁴ On the other hand, the results of these tests also correlated closely with the quantity retained on the $\frac{1}{2}$ -inch screen after the shatter test,⁹⁵ so that Mott and Wheeler reached the conclusion that, "in general . . . cokes for which the $\frac{1}{2}$ -inch index falls below 97.0 may be found to be 'abrada-ble.'"

⁹² See pp. 82-93 of ref. 86.

⁹³ See pp. 109-12 of ref. 67.

⁹⁴ See Table XXV, p. 87, of ref. 86.

⁹⁵ See p. 112 of ref. 67.

⁹¹ Haüsser, F., *Stahl u. Eisen*, 45, 878-85 (1925). See also pp. 80-1 of ref. 67.

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It has been found in the Coal Research Laboratory, by an analysis of steel-plant data, that the correlation between the 2-inch shatter indexes and the 1-inch tumbler index on 139 samples was +0.33, whereas the correlation between the shatter index and the amount remaining on the $\frac{1}{4}$ -inch screen after the tumbler test was only -0.11. Although neither the tumbler nor the shatter test in this comparison was the standard test, the results are probably nearly parallel to those of the standards. Thus, this result indicates that, not only is the tumbler-test result similar to that found by shatter testing when the $\frac{1}{2}$ -inch shatter is compared with the $\frac{1}{8}$ -inch tumbler value as found by Mott and Wheeler, but also the comparison still holds, although not, perhaps, so closely, when the 2-inch shatter-test result is compared with the 1-inch tumbler-test result. On the other hand, the correlation coefficient between the 2-inch shatter and the $\frac{1}{4}$ -inch tumbler results is so low that it is very probable that these quantities measure quite different properties of the coke.

Yancey and his coworkers have recommended a friability index for quoting the results of the tumbler test also,⁸¹ and they show that its use includes the effects of changes in both the 1.05-inch index or "stability factor," and the 0.263-inch index or "hardness factor." In view of the result of the last paragraph, however, it is questionable whether this procedure may not defeat its own end; the quantity remaining on the smallest screen appears to measure most uniquely the property for whose determination the tumbler test supplements the shatter test. This conclusion is supported by the British Standard test,⁹⁰ in which the percentage remaining on an $\frac{1}{8}$ -inch screen is the only quantity reported. The significance of this quantity was determined from experience in blast-furnace

practice,⁹⁶ in which it was found that when this index fell below 74 the driving of the furnaces became more difficult.

When the results of the American standard tumbler test are plotted to arithmetic probability coordinates,⁹⁷ it is found that the results of the sieving on screens having openings of 1 inch or larger tend to fall on straight lines, just as the results of the shatter test do, but that the proportion passing the smaller sieves is very much larger than corresponds to the extension of the line. Thus, it appears that the production of sizes of 1 inch and larger in the tumbler test is due to action very similar to that in the shatter test, in agreement with the results noted by Mott and Wheeler,⁶⁷ by Braunholtz, Nave, and Briscoe,¹⁴ and by Kinney and Perrott.⁷⁰ On the other hand, the production of fines is evidently due to some other mechanism, presumably one of abrasion, so that either the proportion of fines produced, or the deviation of the amount of fines produced from that expected by extension of the straight line representing the size analysis of the larger sizes, may be expected to be an estimate of the susceptibility of the coke to degradation by abrasion and might be expected to be parallel to the results of the Sheffield drum abrasion test.⁹⁴ Bunte and Brückner⁸⁴ found that the percentage remaining on the 40-millimeter sieve after the Micum test was usually but not invariably parallel to the percentage on the same screen after their shatter test, and they considered the departures from the proportional relation between shatter and tumbler test of great significance.

As is true of the shatter test, various small tumbler tests have been developed

⁹⁶ Cochrane, G. D., *J. Iron Steel Inst. (London)*, **97**, 141-50 (1918).

⁹⁷ Lowry, H. H., and Mayers, M. A., *Iron Steel Engr.*, **20**, No. 2, 36-46 (1943).

for the comparison of cokes produced on a laboratory scale. The Nedelmann trommel^{82, 98} is a hammer-mill consisting of a drum 350 millimeters in diameter, 75 millimeters long, having four curved lifters on its internal wall. It also has three swing hammers within the drum, each approximately 25 millimeters long, which are rotated from the central shaft at 55 times the rate of rotation of the drum, which is about 169 rpm. One hundred grams of coke sized between 15 and 20 millimeters is treated in the drum for 1 minute, and the product is sieved on a 10-millimeter screen. The average of three determinations which differ among themselves by not more than 3 percent is reported as the tumbler index. A comparison of this test with the Micum trommel⁸² test is shown in Table VII.

TABLE VII

COMPARISON OF MICUM (LARGE-SCALE) AND NEDELMANN (SMALL-SCALE) DRUM TESTS⁸²

Weight of sample Sizing of sample, mm Sizes reported after test, mm	Micum 50 kg >50		Nedelmann 100 grams 15 x 20	
	+40	-10	+10	-1
Coke 1	85.1	7.6	87.7	8.6
Coke 2	87.1		89.7	6.9
Coke 3	81.5	7.9	82.6	8.0
Coke 4	81.4	8.6	82.8	7.2

Another small-scale test which has been correlated with the results of the Micum trommel has been reported by Šimek and Coufalík.⁹⁹ In this test, the sample of coke (no sample weight or size limits were given) is placed in a drum similar in all respects to the Micum drum, but reduced in all dimensions in the ratio of 3 to 10, and is rotated at 25 rpm for 50 minutes. The authors deduced that the ratio of the

times required in the Micum and their small drums should be in the inverse ratio of the squares of the diameters for equal results in the two tests. Since the Micum is rotated for 4 minutes, the small drum should require 44.4 minutes for the same amount of degradation. However, their results in the small drum, though approximately parallel to the results of the Micum test for different coals, differed consistently from them.

Mott and Shimmura have also reported a small-scale test of abrasion.¹⁰⁰ In this test 4 grams of coke sized between Nos. 5 and 10 I.M.M. sieves were rotated in a brass cylinder 1 inch in internal diameter and 1 inch long at 20 rpm for 30 minutes. The product was screened on 10-, 20-, and 60-mesh sieves, and the percentage passing the 60-mesh was reported as the abrasion index. No correlation of the results of this test with full-scale tests was reported.

(c) Other Abrasion Tests. Several workers have attempted to set up true abrasion tests, either in the hope of developing a useful test for routine work or as a method of calibrating a drum test. These have failed to be useful for more than a research tool because the requirement that a small, shaped sample be used makes representative sampling of large amounts of coke impossible; their value, even as a research tool, is limited because of the differences among different pieces of coke even when produced under carefully controlled laboratory conditions. Mott and Wheeler⁸² and Bähr and Fallböhmer¹⁰¹ used tests in which a smoothed surface of a cube of coke was held against an abrasive wheel under a known pressure, and the weight loss in a fixed time was determined. Mott

⁹⁸ Broche, H., and Nedelmann, H., *Glückauf*, **68**, 770 (1932).

⁹⁹ Šimek, B. G., and Coufalík, F., *Mitt. Kohlenforsch. Inst. Prag*, **2**, 262-79 (1935).

¹⁰⁰ Mott, R. A., and Shimmura, T., *Fuel*, **7**, 486 (1928).

¹⁰¹ Bähr, H., and Fallböhmer, F., *Gas- u. Wasserfach*, **69**, 909-12, 929-32, 943-7 (1926).

and Wheeler used pressures of 1, 2, and 3 pounds per square inch on the faces of a 2-inch cube, with a grinding wheel speed of 1,750 rpm, and held the sample in place for periods of 15 seconds. They found average rates of loss of weight that were independent of the pressure and ranged from about 2 to about 5 grams per 100 square centimeters of surface, but the results were not very precise. Bähr and Fallböhmer used a pressure of 200 grams per square centimeter (2.85 pounds per square inch), a wheel speed of 100 rpm, and times of 3 minutes; they reported their results as the inverse of the weight loss, in grams, from a square centimeter section.

Šimek and Coufalík⁹⁹ also set up a "true" abrasion test in which a circular space 40 millimeters in diameter was exposed to the action of a standardized sand blast for 3 and 6 minutes and the weight loss determined. They found that cokes differed in that some lost more weight from faces parallel to the walls of the oven than from faces transverse to those walls, whereas in others the reverse was true. Mott and Wheeler,⁹² however, found that all their cokes but one lost weight faster from faces parallel to the wall than from transverse faces.

A so-called pressure abrasion test has been developed¹⁰² and rather extensively used in Germany. This test, which approximates the conditions to which coke is exposed in the blast furnace, is illustrated in Fig. 4. The coke, as received at the blast-furnace plant, is charged into the stack and forced out through the weighted bottom doors by a piston driven by feed screws in the same way as the head on a tension-test machine. The pressure required to force the coke out through the bottom doors is nearly independent of the

size of the coke and of its abrasability, and the machine and its operation have been very carefully standardized. The product emerging from the machine is screened on a 30-millimeter round hole sieve, and the percentage passing the sieve is called the "pressure abrasion value."

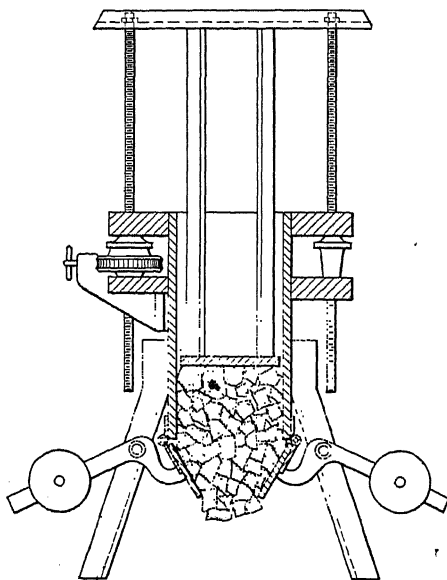


FIG. 4. Wolf pressure abrasion test apparatus.¹⁰²

The bulk density of the coke is observed at the same time as the pressure abrasion test is made by weighing the coke required to fill the machine, whose volume is $\frac{1}{8}$ cubic meter (11.77 cubic feet). No relation was found between the results of the Micum trommel and the Wolf tests. Several examples were given where the Wolf test indicated poor quality of the coke, which was subsequently substantiated by the operation of the blast furnaces, when the tumbler test showed no change in the quality of the coke. Moreover, it was shown that, whereas the tumbler test was quite sensitive to changes in cokes resulting

¹⁰² Wolf, W., *Stahl u. Eisen*, **48**, 33-8 (1928).
Kürner, J., *Feuerungstechn.*, **19**, 194-6 (1931).

from differences in the width of the ovens in which they were made, the results of the Wolf test were practically independent of such effects. If it should be found that correlation of the results of blast-furnace operation with the properties of coke that are usually measured in this country fails to give statistically significant criteria of coke quality, it seems that the Wolf test might be further investigated here to determine whether it may supply the required criterion.

(d) Other Tests of Coke Strength. One of the first tests of coke strength that was used was the determination of its crushing strength, or ultimate strength in compression.^{21, 98, 103} This test was of limited value because, like the true abrasion tests described above, it requires a cut sample which cannot be representative of the coke, and the values obtained vary over wide limits. Moreover, the result of the test does not appear to be significant since the compressive strength of all coke is much greater than any load to which it is subjected in practice; the possible influence of the compressive strength of coke in determining its behavior in use is of low order by comparison with that of its resistance to breakage by shock or its resistance to degradation by abrasion. Hence, this test is seldom used nowadays.

A test, similar in that a known amount of energy is expended, has been standardized by Gabinskii and Badanova.⁷⁵ In this test a weight (5, 10, and 15 kilograms in successive series) is dropped from a height of 1 meter on each of a series of 15 pieces of coke, which are presumed to be representative of the coke tested. In the particular form of the test used by these authors, the increase in surface of the coke

due to crushing was calculated from the size analysis of the crushed coke and the results of the test were expressed as the ratio of the specific surface of the crushed coke to that of the original coke as a function of the amount of work done in kilogram-meters. Although the test may be of value in research on coke properties, it is probably too tedious for general use.

Tests similar to this in principle, however, have been developed by the Northern Coke Research Committee^{15, 104} and in the Coal Research Laboratory¹⁰⁵ to measure the strength of the basic coke substance, rather than that connected with its liability to break along fissures or at points of weakness; they are adapted to the use of the small samples produced in laboratory investigations. The Warren test could also be employed for large-scale samples since a sample of 10 grams of coke crushed to pass a No. 60 and remain on a No. 100 U. S. Standard Mesh Sieve can be representative of as large a volume of coke as may be desired, provided that the sample reduction is properly carried out.⁶⁶ In the Warren test, the sample is ground in a 6-inch-diameter rod mill, 6 inches long, containing a charge of 22 cold-rolled steel rods $\frac{1}{2}$ inch in diameter weighing 3,050 grams, for 150 revolutions of the mill. An investigation of the extent of the new surface formed by milling showed that all the criteria placed a series of cokes in the same order, and so the simplest one, the percentage of the original coke remaining on a 100-mesh screen after grinding, was adopted. This measure of strength was found to increase with the temperature of formation of cokes made from the same coal, in contrast with the shatter index, which decreases as the carbonization tem-

¹⁰³ Perrott, G. St. J., and Fieldner, A. C., *Proc. Am. Soc. Testing Materials*, **23**, II, 475-93 (1923).

¹⁰⁴ Anon., *Fuel*, **16**, 148-51 (1937).

¹⁰⁵ Warren, Wm. B., *Ind. Eng. Chem.*, **27**, 72-7 (1935).

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perature increases. In the Northern Coke Research Committee "micro-strength" test, 2 grams of coke crushed to pass a No. 14 and remain on No. 25 British Standard sieve is charged into a tube 1 inch in internal diameter and with an inside length of 12 inches, with 12 steel balls, $\frac{5}{16}$ inch in diameter. Two such tubes are mounted at right angles to each other and to the axis of a drive shaft, by which they are turned end for end at 25 rpm for 800 revolutions. The results of the test were expressed as the percentage of the original coke remaining on the No. 25 and the No. 72 British Standard sieves. As shown in Table VIII, the micro-strength indexes bear no apparent relation to the results of the shatter or tumbler tests on the same coke. In fact, this test, like the Warren test, is adapted to the measurement of the strength of the basic coke material, not of its conglomeration into pieces of coke.

Density, Specific Gravity, and Pore and Void Volume. The basic test of this group is that of bulk density because the skips supplying coke to blast furnaces are usually loaded by volume rather than by weight. When the apparent density of the coke is also known, the void volume in the bed of coke can be calculated by the relation:

$$v = 1 - \frac{d_b}{62.5g_a} \quad (15)$$

where v is the volume of voids, expressed as a fraction; d_b is the bulk density in pounds per cubic foot, and g_a is the apparent specific gravity of the coke.

The bulk density, or weight per cubic foot, of coke is determined by filling a weighed box of known volume with coke and weighing again, when the bulk density is the weight of the coke divided by the volume of the box in cubic feet. The various standard methods for its determination

TABLE VIII

COMPARISON OF NORTHERN COKE RESEARCH COMMITTEE MICRO STRENGTH WITH RESISTANCE TO SHATTER¹⁰⁴

Coke	Shatter		N.C.R.C.	
	Percent on 2-Inch	Percent on	Percent on No. 25	Percent on No. 72
509	75	90	5	66.5
510	86	93	16	69
511	84	91	11	64.5
512	71	80	11	62.5
513	77	88	14.5	65
514	82	91	16	66
379A Wall ends of full-length pieces	71	86	27.5	73
379B Inner ends of full-length pieces	72	85	15.5	68
57a Lab. coke, 0.2 pound per square inch pressure			0	0
57e External pressure, 3 pounds per square inch			0.5	9.5
57c External pressure, 10 pounds per square inch			7.5	49
57g External pressure, 20 pounds per square inch			13	59

specify that the coke shall be dropped into the box from a shovel, held a short distance, usually 2 inches, above the edge of the box, and that the box shall not be shaken, dropped, tapped, or tamped in any way while the coke is being added. The coke is leveled by hand, and the leveling is checked by laying a straight edge across the upper edges of the box. The American standard¹⁰⁶ calls for the use of an 8 cubic foot box, 2 feet on each inside edge. It specifies that for coke larger than 1 inch a sample of not less than 300 pounds shall be taken; for smaller coke, not less than 50 pounds is required for a sample. For proper interpretation of the result, a moisture determination and size analysis are required. A 1 cubic foot box, 12 inches on each side edge, may be used for the determination when the coke is smaller than 1 inch. The British standard⁶¹ specifies a 2 cubic foot box, 15½ inches on each inside edge, and requires that the coke for the test be taken from the shattered sample produced by the application of the standard shatter test. The use of the sample from the shatter test may be expected to give higher values, on the average, for the British test than for the American test run on comparable cokes. Because of the possible errors introduced by wall effects when the bulk density of large coke is determined, even in so large a container as an 8 cubic foot one, the United States Steel Corporation¹⁰⁷ also gives a method for making this determination on a railroad car full of coke. This precaution is supported by the results obtained by Killing,¹⁰⁸ who observed a bulk density 3

¹⁰⁶ Am. Soc. Testing Materials Standard D292-29.

¹⁰⁷ U. S. Steel Corporation, Chemists' Committee, *Sampling and Analysis of Coal, Coke and By-Products*, 3rd ed., Carnegie Steel Co., Pittsburgh, 1929, p. 38.

¹⁰⁸ Killing, A., *Stahl u. Eisen*, 51, 901-5 (1931).

percent higher in a railroad car of 38 cubic meter capacity than was obtained in a 1 cubic meter measure for the same coke.

Because of the irregularity and porosity of coke, its apparent density may vary, depending on the method of its determination. For this reason, it is desirable that the method for this determination be described; if a standard method is followed, any deviation from the standard should be mentioned. Two methods are in general use: one is applicable to large samples that may be made representative of commercial shipments; the other requires individual treatment of each particle and so is adapted only to laboratory work.

The British Standards Institution has refused, thus far, to set up a specification for a standard method of determining apparent specific gravity because of the difficulties mentioned above, but the A.S.T.M. does give a standard method for the determination.¹⁰⁹ About 25 pounds of coke, larger than 1 inch, is suspended in a wire cage after being weighed, then immersed in a large vessel with an overflow spout, which has been filled to the overflow with water with the cage suspended in the vessel. After the coke has been immersed for 15 minutes with occasional shaking to dislodge air bubbles, the water is allowed to overflow down to its original level, the overflow being caught in a tared bucket. The coke is then withdrawn and, after draining for 1 minute, is weighed wet, and the amount of water in the overflow bucket is determined. The apparent specific gravity is determined by

$$g_a = \frac{A}{B + (C - A)} \quad (16)$$

where A is the weight of the dry coke, B the weight of water displaced by the coke,

¹⁰⁹ Am. Soc. Testing Materials Standard D167-24.

and C is the weight of wet coke. Essentially similar methods have been used by the U. S. Steel Corporation,¹¹⁰ and by Mott and Wheeler,¹¹¹ except that these authorities determined the weight of water displaced by weighing the coke in the water, rather than by catching and weighing the overflow, and in the method described by Mott and Wheeler the water in which the coke was immersed was boiled for $\frac{1}{2}$ hour to expel all the air in the "open" pores. Results by this method were compared with those obtained by the normal boiling method, and average deviations from the mean about $\frac{1}{8}$ to $\frac{1}{2}$ as great were observed; the mean values agreed within 2 percent. No comparison between the results obtained by the American method, without boiling, and those obtained when the displacing liquid is boiled is known. In view of the length of time that must be taken to cool the large bath of water, it seems hardly likely that the accuracy of the results is increased sufficiently by this procedure to justify it. Furthermore, the possibility of the introduction of serious errors by failure to cool quite down to the standard temperature is greatly enhanced.

Another common method for determining apparent specific gravity involves the coating of individual pieces of coke by paraffin and the determination of the volume of water displaced by the smooth-surfaced bodies thus produced.¹¹² This involves the handling of many pieces separately in order to obtain results representative of a large consignment of coke and thus is not suitable for general use. Sometimes, though

usually only on a laboratory scale,¹¹³ the weight of mercury displaced by coke is determined. This measurement is based on the high surface tension of mercury which is so great that the mercury is assumed not to enter even large pores in the coke; but the facts that the coke floats in mercury and that it is impossible to observe whether all air bubbles have been displaced cast doubt on results obtained in this way.

It is to be noted that the need for high accuracy in the determination of apparent density is great or small depending on whether the value obtained is to be used for the determination of the porosity of the coke, defined by:

$$p = 1 - \frac{g_a}{g_t} \quad (17)$$

where p is the porosity expressed as a fraction and g_t is the true density, or for the determination of void volume according to equation 15. The uncertainty in the determination is equivalent to a somewhat doubtful determination of the boundaries of the geometrical figure which completely encloses the average coke particle. This uncertainty would result in a large proportional uncertainty in the pore volume of the coke, all of which is included within the geometrical boundary, but the pore volume would be negligible by comparison with the much larger volume which exists between pieces. Thus, if, as appears likely from the considerations dealt with on pages 867-70 of this report, the void volume in a bed is found to be of great significance, and the porosity of coke of very minor significance, in determining its suitability for use in the blast furnace a determination of apparent specific gravity of even low accuracy may be adequate.

The true specific gravity is usually deter-

¹¹⁰ See pp. 59-60 of ref. 107.

¹¹¹ See pp. 73-7 of ref. 67.

¹¹² Nave, G. M., *J. Soc. Chem. Ind.*, **46**, 158-9T (1927). Hoffmann, F. G., *Brennstoff-Chem.*, **11**, 297-9 (1930). Stadnikoff, G., *ibid.*, **11**, 330-1 (1930).

¹¹³ Drakeley, T. J., and Wilkins, E. T., *J. Soc. Chem. Ind.*, **50**, 334T (1931).

mined by charging a weighed portion of the finely ground coke to a tared bottle of known volume, partly filling it with water, boiling either on a hot plate or by means of reduced pressure to eliminate air from the pores of the coke, cooling, filling with air-free distilled water, and weighing. Specific instructions for carrying out the test are given by the A.S.T.M.¹⁰⁹ and the British Standards Institution⁶¹ and need not be repeated here. Questions have centered about the correct size of coke, the desirability of liquids other than water, and whether or not wetting agents should be added to the water.¹¹⁴ Hiles and Mott found better reproducibility of results using coke crushed to pass a 60-mesh screen than with that passing a 200-mesh screen. They also showed that substituting organic liquids for water as the displacing fluid made the observations less precise owing to errors of fluid temperature, and that the use of wetting agents led to erroneous results because of adsorption by the coke.

Smith and Howard¹¹⁵ have shown that all methods of determining density by filling the pores of as porous a material as coke with a liquid are open to error because of failure of the liquid completely to penetrate the pores, and they described a method in which helium serves as the displacing fluid. They showed that large differences in the density of very finely porous materials, such as activated charcoal, may be observed using helium and a liquid, but that, for high-temperature cokes, at least, the differences were small, of the order of 0.03 in the specific gravity, and

relatively constant. The determination of true density by displacement with helium is, undoubtedly, a valuable research tool, but it is not to be recommended for routine work.

A measurement related to the porosity, which is usually determined from the true and apparent specific gravities by means of equation 17, is the "permeability" of coke, i.e., the relation between the pressure required to force air (or other gas) through the pores of the coke and the volume of gas flowing.¹¹⁶

REACTIVITY

An almost infinite variety of reactivity tests have been elaborated for coke, depending on the particular application of coke in which the worker was interested or on his personal idiosyncrasies and preferences. The writer has previously reviewed a portion of the literature on this subject,¹¹⁷ and the earlier work was very thoroughly reviewed by Mezger and Pistor¹¹⁸ and by Agde and Schmitt.¹¹⁹ In general, the methods can be divided into two classes: those using laboratory-scale methods, in which an attempt is made to estimate the rate of a chemical reaction between coke and some oxidizing gas; and

¹¹⁶ Wüst, F., and Rütten, P., *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **5**, 1-12 (1924). Swietoslawski, W., and Chorazy, M., *Przemysł Chem.*, **18**, 574-9 (1934). Chorazy, M., and Chmielinski, T., *ibid.*, **19**, 113-22 (1935). Golovaty, R. N., *Coke & Chem. (U.S.S.R.)*, **6**, No. 2-3, 15-20 (1936). Idashkin, S. I., *ibid.*, **6**, No. 9, 71-2 (1936); *Chimie & industrie*, **35**, 459 (1937).

¹¹⁷ Mayers, M. A., *Congr. chim. ind.*, 15th Congr., Brussels, 1935, **2**, 667-76 (1936); *Carnegie Inst. Tech., Coal Research Lab. Contrib.* **36** (1936), 9 pp.

¹¹⁸ Mezger, R., and Pistor, F., *Die Reaktionsfähigkeit des Kokes*, W. Knapp, Halle, 1927, 88 pp.

¹¹⁹ Agde, G., and Schmitt, H., *Theorie der Reaktionsfähigkeit von Steinkohlenkoks*, W. Knapp, Halle, 1928, 165 pp.

¹¹⁴ See Nave, G. M., in ref. 112. See also Braunscholtz, W. T. K., Nave, G. M., and Briscoe, H. V. A., in ref. 79. Neumann, B., Gross, W., Kremser, L., and Schmidt, J., *Brennstoff-Chem.*, **15**, 161-5 (1934). Hiles, J., and Mott, R. A., *Fuel*, **16**, 64-71 (1937).

¹¹⁵ Smith, R. C., and Howard, H. C., *Ind. Eng. Chem.*, **34**, 438-41 (1942).

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those using large-scale furnaces and lump coke, in which the observation covers the rate of burning of the fuel or the composition of the gas rising from the bed, both of which, as has been shown elsewhere,^{17, 120} are only slightly dependent on the rates of the chemical reactions concerned but are greatly influenced by the physical conditions under which the reaction proceeds. Thus, the term "reactivity" has been used to cover tests of two widely different properties; for clearness in this report, it will be restricted to designate only the laboratory-scale tests, and the others will be referred to as "burning" tests.

In contrast with this too broad application of the term, most of those who have been concerned with laboratory-scale tests have divided them into several groups. They have reserved the term "reactivity" for tests in which the oxidizing gas was carbon dioxide¹²¹ or, occasionally,

¹²⁰ Mayers, M. A., *Chem. Revs.*, **14**, 31-53 (1934).

¹²¹ Clement, J. K., *Univ. Ill. Eng. Exp. Sta., Bull.* **30** (1909), 47 pp. Clement, J. K., Adams, L. H., and Haskins, C. N., *U. S. Bur. Mines, Bull.* **7** (1911), 58 pp. Rhead, T. F. E., and Wheeler, R. V., *Trans. Chem. Soc.*, **101**, 831 (1912). Fischer, F., Breuer, P. K., and Broche, H., *Brennstoff-Chem.*, **4**, 33-9 (1923). Häusser, F., *Stahl u. Eisen*, **43**, 903-7 (1923). Arend, J. P., and Wagner, J., *Rev. mét.*, **21**, 585-99 (1924). Bähr, H., *Stahl u. Eisen*, **44**, 1-9, 39-48 (1924); Koppers, H., *ibid.*, **44**, 691-4 (1924). Evans, E. C., *Colliery Guardian*, **130**, 143-4 (1925). Leflier, J. A., *Jernkontorets-Ann.*, **110**, 165-208 (1926). Brender à Brandis, G. A., and LeNobel, J. W., *Het Gas*, **47**, 37-47 (1927). Nettlenbusch, L., *Brennstoff-Chem.*, **8**, 37-41 (1927). Dent, F. J., *Gas J.*, **184**, 199-200 (1928). Jungbluth, K., and Klapp, K., *Giesserei*, **16**, 761-2, 787-800 (1929). Oshima, Y., and Fukuda, Y., *J. Soc. Chem. Ind. (Japan)*, **32**, Suppl. Binding, 208-10, 226-7, 251-2 (1929); *Fuel*, **9**, 5, 200 (1930). Seidenschur, F., and Jäppelt, A., *Brennstoff-Chem.*, **10**, 195-8 (1929). Rieffel, M., *Chimie & industrie*, **26**, 280, 531 (1931). Broom, W. E. J., and Travers, M. W., *Proc. Roy. Soc. (London)*, **A135**, 512-37 (1932). Bolland, C. B., and Cobb, J. W., *J. Soc. Chem. Ind.*, **52**, 153-9T (1933). Broche, H., and Nedelmann, H., *Stahl u. Eisen*,

steam;¹²² and "combustibility" for tests in which air or oxygen was used and the extent of reaction observed by weighing or gas analysis;^{81, 123} and have kept "ignition point" for tests in which air or oxygen was used and the extent of reaction observed by temperature measurement.¹²⁴ This dif-

53, 144-7 (1933). Collina, C., and Giordano, I., *Ist. chim. ind. sez. combustibili, Politecnico Milano*, **4**, 253-64 (1932-3). Kassler, R., *Chimie & industrie*, Special No., 315-26, June 1933. Namikawa, T., *J. Soc. Chem. Ind. (Japan)*, **36**, Suppl. Binding, 242-3 (1933). Roberts, J., *Colliery Engr.*, **10**, 220-2, 230 (1933). Cobb, J. W., *Chaleur & ind.*, **15**, No. 167, 377-86 (1934). Gevers-Orban, E., *Rev. universelle mines*, **10**, 313-20, 347-52, 376-86 (1934). Müller, W. J., and Jandl, E., *Brennstoff-Chem.*, **15**, 347-51 (1934). Reis, A., *Chimie & industrie*, **33**, 1297-306 (1935). Sabonadier, J., *J. usines gaz*, **59**, 546-59 (1935). Petrenko, I. G., *Coke & Chem. (U.S.S.R.)*, **6**, No. 10, 61-5 (1936). Šimek, B. G., *Mitt. Kohlenforsch. Inst. Prag*, **3**, 95-106 (1937).

¹²² Pexton, S., and Cobb, J. W., *Gas J.*, **167**, 161-9 (1924). Key, A., and Cobb, J. W., *J. Soc. Chem. Ind.*, **49**, 439-44T (1930). Dolch, P., *Brennstoff-Chem.*, **14**, 261-3 (1933). Brewer, R. E., and Reyerson, L. H., *Ind. Eng. Chem.*, **27**, 1047-53 (1935), **26**, 734-40 (1934). Namikawa, T., *J. Soc. Chem. Ind. (Japan)*, **38**, Suppl. Binding, 405-7 (1935). Krüger, C., and Melhorn, G., *Brennstoff-Chem.*, **19**, 157-69, 257-62 (1938).

¹²³ Koppers, H., *Stahl u. Eisen*, **42**, 569 (1922). Broche, H., *Brennstoff-Chem.*, **4**, 343-6 (1923). Fieldner, A. C., *Chem. & Met. Eng.*, **29**, 1052-7 (1923). Häusser, F., in ref. 121. Holtzhaus, C., *Mitt. Dortmunder Union*, **1**, 194-236 (1926). Braunscholtz, W. T. K., Nave, G. M., and Briscoe, H. V. A., in ref. 79. Dengg, R. A., *Fuel*, **7**, 152-4 (1928). Kreulen, D. J. W., *Brennstoff-Chem.*, **10**, 148-53, 168 (1929). Berker, E. M., *Coke & Chem. (U.S.S.R.)*, **1931**, Nos. 2-3, 149-54. Godbert, A. L., *Safety Mines Research Board (London), Paper 68* (1931), 9 pp. Blayden, H. E., and Riley, H. L., *Gas World*, **99**, Coking Sect., 116-21 (1933). Newall, H. E., *Fuel*, **17**, 260-5, 292-9 (1938). Finiston, H. M., *J. West Scotland Iron Steel Inst.*, **47**, 15-31 (1939).

¹²⁴ Arms, R. W., *Univ. Ill. Eng. Exp. Sta., Bull.* **128** (1922), 61 pp. Bunte, K., and Kölmel, A., *Gas- u. Wasserfach*, **65**, 592-4 (1922). Parr, S. W., and Staley, W. D., *Ind. Eng. Chem.*, **19**, 820-2 (1927). Swietoslawski, W., and Roga, B., *Przemysł Chem.*, **12**, 18-31 (1928). Agde, G., and Schnittpahn, M., *Brennstoff-Chem.*, **10**, 257-61, 282-7 (1929). Berl, E., and Weingärt-

ferentiation appears to be quite unnecessary since it has been abundantly shown that all the methods mentioned are simply different devices for measuring the same property. By comparing series of cokes of different reactivities, it has been shown that the reactivity with air is parallel to the ignition point,¹⁹ and the reactivity to carbon dioxide¹²⁵ and to steam¹²⁶ is parallel to change in the ignition point; that the reactivity to air, to oxygen, and to carbon dioxide is parallel to changes in the ignition temperature;^{101, 127, 128} and that the reactivities to air, to oxygen, to carbon dioxide, and to steam are all parallel.^{129, 130} Finally, all the methods of attack were tried and found to give parallel results in the work of the South Metropolitan Gas Company.¹³¹ Hence, only a few examples of reactivity tests will be described, since the results of any one of the tests, executed

with adequate precautions, is convertible, theoretically, at least, into any of the others.

Reactivity to Carbon Dioxide. Perhaps the best developed of the methods depending on the measurement of the rate of the reaction



is that of Agde and Schmitt¹¹⁹ as modified by Müller and his collaborators.^{132, 133} In all these tests, the reactivity is reported as the value of

$$R = 100 \frac{x}{a} \quad (18)$$

where R is the percent reactivity, x is the volume of carbon dioxide reduced to carbon monoxide in a given time, and a is the volume of carbon dioxide supplied in that time. It has been shown^{117, 134} that this expression for reactivity does not give results that are proportional to the reaction rates of the fuels tested except when R is quite small; when it is used, the differences between fuels of high reactivity are greatly underestimated. From this point of view, the last method developed by Müller and Jandl¹³³ is much to be preferred to the earlier ones, since the values of R for a given coke obtained by its use are much smaller than the value given by the earlier method, even though the authors refer to the later method as a "rapid" and the earlier as the "exact" method. The determination is made at only one temperature, although it has been shown¹³⁵

ner, E., *Z. physik. Chem.*, **A161**, 315-24 (1932). Kreulen, D. J. W., *Fuel*, **13**, 55-9 (1934). Brown, C. R., *Fuel*, **14**, 14-8, 56-9, 80-5 (1935). Bunte, K., and Windorfer, K., *Gas- u. Wasserfach*, **78**, 697-701, 720-5, 737-43 (1935). Gynge, E. S., *Fuel*, **14**, 254-8 (1935). Brown, W. S., and Jones, J. H., *J. Soc. Chem. Ind.*, **55**, 81-6T (1936). Markovskii, L. Ya., *Khim. Tverdogo Topliva*, **7**, 574-85 (1936). Roberts, J., *Gas. J.*, **213**, 372-4 (1936). Heinze, R., and Farnov, H., *Braunkohle*, **36**, 277-83, 300-2 (1937). Bunte, K., Brückner, H., and Bender, W., *Gas- u. Wasserfach*, **81**, 178-83, 200-3 (1938). Jostes, F., and Siebert, K., *Oil, Kohle, Erdöl, Tecr.*, **14**, 919-31 (1938). Klukowski, A., and Jarzynski, A., *Przemysł Chem.*, **22**, 406-11 (1938).

¹²⁵ Drakeley, T. J., *J. Soc. Chem. Ind.*, **50**, 317-30 (1931).

¹²⁶ Bunte, K., and Giessen, A., *Gas- u. Wasserfach*, **73**, 241-7 (1930).

¹²⁷ Bunte, K., *Z. angew. Chem.*, **39**, 132-8 (1926). Müller, W. J., and Jandl, E., *Brennstoff-Chem.*, **19**, 27-9 (1938).

¹²⁸ Davis, J. D., and Fieldner, A. C., *Proc. Am. Gas Assoc.*, **1935**, 636-59.

¹²⁹ Davis, J. D., and Greene, J. W., *ibid.*, **1926**, 1160-4. Davis, J. D., and Reynolds, D. A., *Ind. Eng. Chem.*, **20**, 617-21 (1928).

¹³⁰ Neumann, B., Kröger, C., and Fingas, E., *Gas- u. Wasserfach*, **74**, 565-72 (1931).

¹³¹ See pp. 10-37 of ref. 51.

¹³² Müller, W. J., and Courard, W., *Brennstoff-Chem.*, **11**, 125-8 (1930). Müller, W. J., and Jandl, E., *ibid.*, **12**, 187-91 (1931).

¹³³ Müller, W. J., and Jandl, E., *ibid.*, **19**, 45-8 (1938).

¹³⁴ King, J. G., and Jones, J. H., *J. Inst. Fuel*, **5**, 39-55 (1931). See also Key, A., and Cobb, J. W., ref. 122.

¹³⁵ Blakeley, T. H., and Cobb, J. W., *Inst. Gas Engrs., Commun.*, **104** (1934), 49 pp.; *Gas J.*, **208**, 351-3, 526-7, 748-9 (1934). Mayers, M. A., *J. Am. Chem. Soc.*, **612**, 2053-8 (1939).

that the temperature coefficient of the reaction is quite as important a characteristic of the fuel as the absolute magnitude of the reaction rate at a given temperature. Thus, it is evident that the method of Müller and Jandl leaves something to be desired from a theoretical point of view; on the other hand, their apparatus has been developed to a high degree of con-

by the necessity for the reacting gas to diffuse to the reaction surface.¹³⁷ The 2 cubic centimeter sample of coke, ground to pass a sieve having 2,500 meshes per square centimeter (approximately No. 120) and to remain on one of 4,900 meshes per square centimeter (approximately No. 170), is held in a quartz boat with a cross-sectional area of 25 square centimeters, which is in-

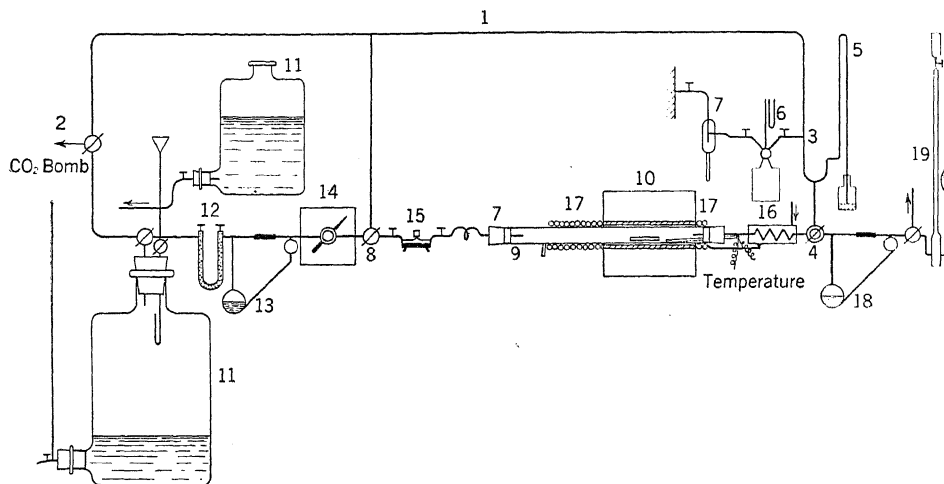


FIG. 5. Diagrammatic layout for reactivity test. Müller-Jandl rapid method.¹³⁵

venience and precision, being approached in precision, probably, only by that developed by the Fuel Research Board.¹³⁶

In this method, the apparatus for which is illustrated in Fig. 5, a constant stream of purified carbon dioxide, controlled by the gasometer 11 and the micro stopcock 14, passes through drying tubes 12 and 15 and a flowmeter 13, into the furnace tube 9, a quartz tube of 35-millimeter bore, 650 millimeters long, at a rate of 2 liters per hour. It may be noted that this rate is probably too low to eliminate completely the physical resistance to reaction set up

serted into the cool end of the furnace tube and remains there until the apparatus has been swept free of air, when it is pushed down into the center of the hot zone of the furnace, which is maintained at $900 \pm 5^\circ \text{C}$. Both ends of the furnace tube are cooled by lead tubing wound around it, through which water is circulated. The gas leaving the furnace passes through a water-cooled coil, through a second flowmeter, and then either to the atmosphere or to an azotometer for determining when the apparatus is air-free. The other connections shown are for securing the air-free condition, and their functions are de-

¹³⁶ Jones, J. H., King, J. G., and Sinnatt, F. S., *Dept. Sci. Ind. Research (British) Fuel Research. Tech. Paper 18* (1927), 32 pp.

¹³⁷ Mayers, M. A., *J. Am. Chem. Soc.*, **56**, 70-6 (1934).

scribed in the reference. The two flowmeters make possible continuous reading of the gas composition if the appearance of small amounts of gas distilled out of the coke can be neglected. It is found that the calculated R increases very rapidly from the time of starting the test to a sharp peak after 1 to 2 minutes, from which it decreases rapidly to a practically constant value, after 10 minutes, which remains unchanged, or decreases only slightly, until 30 minutes after the start of the test, when it is considered complete. The constant value which appears after 10 minutes is taken as the criterion of reactivity of the coke.

Modified Ignition-Point Method. An altogether different method of determining reactivity has been developed in the Coal Research Laboratory,^{117, 138} and a similar one independently by Seyler and Jenkins.¹³⁹ In both, the rate of reaction is measured by the rate of heat evolution when a stream of oxygen or air is passed through the heated sample; they are thus developments of the ordinary methods of measuring "ignition" temperature.¹²⁴ It is recognized that ignition temperature, in the sense that this temperature is a point below which combustion reactions do not proceed, is an erroneous conception. Nevertheless, the point at which the rate of self-heating by a sample, heated by an external source, becomes great enough so that the sample temperature overtakes the source temperature is a significant one, which may be combined with other ob-

servations to determine reaction rates at various temperatures.

In the Coal Research Laboratory test, the supplementary datum required in addition to the observation of the crossing point in order to calculate the reaction rate is the rate of rise in temperature of the coke sample at this point. It can be shown that the reaction rate is proportional to this quantity, the constant of proportionality being the ratio of the heat evolved per unit mass of the coke reacting, to the specific heat of the coke. As there is some doubt about the magnitudes of these quantities, especially the last, the results of the test are reported as the rates of rise of temperature; that these can be converted to reaction rates with fair accuracy, however, is shown by the agreement of the effective ignition temperatures for fuel-bed conditions calculated from such results with the magnitudes observed experimentally.¹⁴⁰ The crossing point and, hence, the temperature at which the reaction rate is observed can be varied, for the same sample, by changing the rate of heating the furnace or by changing the concentration of oxygen in the gas stream flowing through the sample. Thus, the dependence of the reaction rate on temperature can be determined; it is found experimentally that this dependence is accurately expressed by the Arrhenius equation, so that a graph of the logarithm of the reaction rate (or of the rate of temperature rise at the crossing point) against the inverse of the absolute temperature at which the crossing is observed gives a straight line.

It is convenient to characterize cokes by the temperatures at which the reaction rates of samples in the Coal Research Laboratory test become great enough to pro-

¹³⁸ Sebastian, J. J. S., and Mayers, M. A., *Ind. Eng. Chem.*, **29**, 1118-24 (1937). See also Klukowski, A., and Jarzynski, A., in ref. 124. Godbert, A. L., and Belcher, R., *17th Ann. Report Safety Mines Research Board (London)*, 1939, p. 44. Sherman, R. A., Pilcher, J. M., and Ostborg, H. N., *Am. Soc. Testing Materials, Bull.* **112**, 23-34 (1941).

¹³⁹ Seyler, C. A., and Jenkins, T. E., *Colliery Guardian*, **156**, 47-50, 71-3 (1937).

¹⁴⁰ Mayers, M. A., and Landau, H. G., *Ind. Eng. Chem.*, **32**,

duce fixed rates of temperature rise, when two values of this quantity define both the magnitude of the reaction rate at a given temperature and its rate of change with temperature. The values of rate of rise chosen for this purpose are 15° per minute, which is near the crossing point observed with the apparatus now in use, when oxygen is the reacting gas; and 75° per minute, which is near the point observed when air is used. Values of these quantities, T_{15} and T_{75} , observed for various coals and cokes are given in Table IX.

TABLE IX

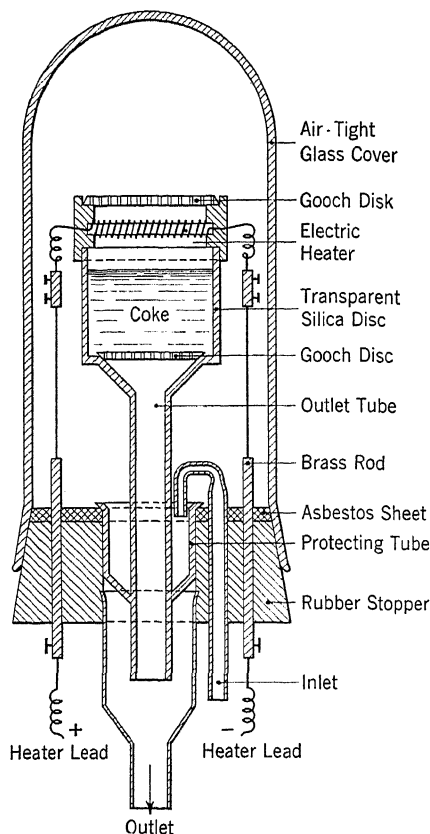
REACTIVITY BY COAL RESEARCH LABORATORY METHOD¹³⁸ T_{15} AND T_{75} FOR VARIOUS COALS AND COKES

Fuel	T_{15} °C	T_{75} °C
Illinois No. 6 Seam Coal	180	225
Pittsburgh Seam coal	230	285
Pocahontas No. 3 Seam coal	245	295
Anthracite	310	425
Semicoke	205	260
Foundry coke		
Undercarbonized	270	390
Well carbonized	500	565
Blast-furnace cokes		
A	455	520
B	500	565
C	550	600

It is believed that the apparatus used for the determination can be improved over that described by Sebastian and Mayers, but the principle involved has been accepted tentatively by Subcommittee XVI on Ignitibility of Coal and Coke, R. A. Sherman, Chairman, of A.S.T.M. Committee D-5, as a basis on which to develop a standard test of reactivity.

The Critical Air Blast. A third method of determining reactivity, which has achieved great popularity in England, is

the critical-air-blast method, developed by the Northern Coke Research Committee.¹⁴¹ In this method, a sample of coke sized between 10 and 20 mesh, I.M.M. standard, is filled to a constant level in the container

FIG. 6. Apparatus for critical-air-blast test.¹⁴¹

illustrated in Fig. 6. Air, preheated by a constant energy supply to the electric heater above the sample, is passed down through the sample, until it is completely ignited, at a rate of 0.150 cubic foot per

¹⁴¹ Blayden, H. E., Noble, W., and Riley, H. L., *J. Inst. Fuel*, **7**, 139-49 (1934). Askey, P. J., and Doble, S. M., *Fuel*, **16**, 359-60 (1937). Brewin, W., and Thompson, J. K., *ibid.*, 361-5 (1937). See also pp. 167-9 in ref. 67.

minute, when the rate is reduced to a value near the expected value of the C.A.B. If the coke remains alight for 20 minutes, the apparatus is cooled and the test repeated with a new sample, using a value of air rate after ignition 0.002 cubic foot per minute lower than before. On the other hand, if the coke goes out in less than 10 minutes, the next trial is run with an air rate higher than the previous one. Thus, two values of air rate are found, differing by 0.002 cubic foot per minute, one of which will keep the coke alight for more than 10 minutes, and the other of which will not. The average of these is reported as the C.A.B.

Although it does not appear at first glance that there is any relation between the value of the C.A.B. and the reactivity as defined above, it was found that the results of a similar test¹⁴² were parallel to determinations of ignition temperature made in the same apparatus. Application of the results of mathematical analysis of fuel-bed conditions^{16, 140} shows that, though a variety of factors will affect the minimum rate of burning when the rate of ignition vanishes, all except the ignition temperature of the fuel under the conditions of test will remain nearly constant when the size and packing of the fuel are held constant, so that the principal variable remaining is only the reactivity of the fuel. The simple one-dimensional analysis referred to, however, cannot estimate exactly the contributions of the various factors which determine the C.A.B., since it takes no account of heat loss to the sides of the bed. That this is an important factor in the determination is shown by the results of Askey and Doble,¹⁴¹ who found that the value of the C.A.B. was lower, the larger the diameter of the apparatus in which the test was conducted, a result that is, quali-

tatively at least, in accord with theoretical expectations.

"Burning" Tests of Combustion Characteristics. "Burning" types of tests of reactivity have been of two kinds: in one, the burning takes place by pure overfeed action,¹⁴³ so that the tests are similar to those pioneered by Kreisinger, Augustine, and Ovitz;¹⁴⁴ in the other, the burning takes place by pure underfeed action,¹⁴⁵ so that these tests are similar to that developed by Nicholls.¹⁴⁶ In the first type of test the emphasis is on the rate of consumption of fuel and the analysis of the gases and the temperatures at various points in the fuel bed; in the second, the significant measurement is the rate of advance of the zone of ignition or the time required for it to strike through the bed. The analysis appropriate to the latter conditions has been given elsewhere;^{16, 140} since it is rather complicated it will not be repeated. It should be noted, however, that a nomogram is given in the last reference by means of which the significant characteristics of the fuel can be estimated if enough experimental data are available, although they are not in the tests as usually performed. Moreover, just as in the C.A.B. test, discussed above, the results are liable to distortion because of the effect of heat losses from the sides of the apparatus,

¹⁴³ Mott, R. A., and Wheeler, R. V., pp. 117-40 of ref. 86 and pp. 132-56 of ref. 67. Werkmeister, H., *Arch. Wärmewirt.*, **12**, 225-32 (1931). Speckhardt, G., *Glückauf*, **72**, 225-31 (1936).

¹⁴⁴ Kreisinger, H., Ovitz, F. K., and Augustine, C. E., *U. S. Bur. Mines, Tech. Paper* **137** (1916), 76 pp.

¹⁴⁵ Rosin, P., Kayser, H. G., Fehling, H. R., *Ber. Reichskohlenrats* D51, 1935, 47 pp. Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel*, **9**, 24-9 (1935), **11**, 117-22, 129-33 (1937), **12**, 87-95 (1938). Rosin, P., and Fehling, H. R., *ibid.*, **11**, 102-17 (1937).

¹⁴⁶ Nicholls, P., *U. S. Bur. Mines, Bull.* **378** (1934), 76 pp. Nicholls, P., and Eilers, M. G., *Trans. Am. Soc. Mech. Engrs.*, **56**, 321-36 (1934).

¹⁴² Holmes, C. R., and Davis, J. D., *Ind. Eng. Chem.*, **28**, 484-8 (1936).

an effect which is not taken account of in the analysis and which may be quite significant for units as small as most of those tested.

Although these tests, in the past, have usually been made on coal rather than on coke, they are equally adapted to measurements on coke, so that a brief description is probably justified. In the Rosin test,¹⁴⁵ coal is charged into a tube 50 millimeters (2 inches) in diameter, heavily insulated on the outside; a measured stream of air is passed up through a grate supporting the fuel, and the fuel is ignited either by preheating the air or by radiation from a gas-heated hot plate radiating to the top surface of the fuel. Temperatures are measured at several levels in the charge, and the time required for ignition under various conditions of hot-plate and air temperature and air velocity are observed by noting the times at which a few particles begin to glow and at which rapid combustion of the volatile matter begins. The method of Dunningham and Grumell is, perhaps, somewhat closer to the conditions of technical firing, in that a pot-type furnace 12 inches in diameter is used, and the air for combustion is not preheated, ignition being accomplished solely by means of an electric heater radiating to the top of the fuel bed.

The measurements by the method of overfeed firing also have been applied most frequently to coal, but they have been used for coke, as well. This test is, essentially, a more refined edition of the "salamander" test common at steel plants but seldom, if ever, described in the literature. The observations usually include gas analysis and, sometimes, temperatures at several levels in the fuel bed and just above the bed. Mott and Wheeler^{143, 147} observed the following

points: the average rate of combustion, the distance from the grate at which free oxygen disappeared, the average carbon monoxide in the gas 12 inches above the grate, the maximum temperature and its distance above the grate 3 hours after the start of the test, and the average temperature in the lower 15 inches of the bed at this time. In these tests, coke was charged to a pot-type furnace, 12 to 26 inches in diameter, and a constant measured stream of air was passed up through the fuel which was ignited from the bottom in a standardized manner, either by means of auxiliary gas burners or by a standard weight of sticks. The fuel was sized within close limits if a comparison of its chemical properties was desired, or it was fired in the sizing in which it was received if an overall measure of its probable behavior in specific equipment was sought. Speckhardt,¹⁴³ in fact, made an attempt to estimate the changes in sizing of the fuel as it passes down through the furnace from the results of the Wolf test¹⁰² on the same sample.

Where complete gas analyses at enough levels are given, the results of such tests may be analyzed in terms of the effective rates of the gasification reaction.^{146, 148} When the amount of volatile matter remaining in the coke is small enough so that its combustion is effectively that of carbon (i.e., the gases in the bed consist to all but a negligible extent of oxygen, carbon dioxide, and carbon monoxide), the quantities

$$\frac{O_2}{1 - \frac{1}{2}CO} \quad \text{and} \quad \left[42 - \frac{CO}{1 - \frac{1}{2}CO} \right]$$

where O_2 and CO are the percentages by volume of oxygen and carbon monoxide in the gas, when plotted on semilogarithmic

¹⁴⁷ *Preprints of the Symposium on the Combustion of Solid Fuels*, Boston meeting of Amer-

¹⁴⁸ Furnas, C. C., *Ind. Eng. Chem.*, **28**, 498-502 (1936).

paper against the distance above the grate give straight lines if the effective reaction rates, μ_1/G and μ_2/G , are constant. Suitable data for making this analysis were given by Mott and Wheeler^{143, 147} and Nicholls,¹⁴⁹ some data from the latter being shown in Fig. 7. It will be observed that the lines representing the rate of reaction of oxygen, given in Fig. 7A, are not well determined by the data because the oxygen was consumed so rapidly that it was found at only two or three levels in the bed. Thus, the determination of μ_1/G , represented by the slope of this line, is not very precise. On the other hand, the values of μ_2/G , the slopes of the lines shown in Fig. 7B representing the changes in car-

bon monoxide content of the gas, are quite adequately determined when they remain constant throughout the bed. Though this appears to be true for several of the cokes, it is not invariably true (see especially lines designated *U* and *R*). In these two lines there is a sharp increase of the slope, corresponding to a much higher value of the reaction rate coefficient, in the neighborhood of 4½ inches above the grate. This may be tentatively explained on either of two grounds: the region in which the increase is observed is that of maximum temperature in the bed, so that if the rate of reaction is partly determined by chemical resistance a higher reaction rate might be expected in this region, especially from cokes having a high characteristic temperature coefficient; on the other hand, the re-

¹⁴⁹ Nicholls, P., Brewer, G. S., and Taylor, E., *Proc. Am. Gas Assoc.*, 1926, 1129-43.

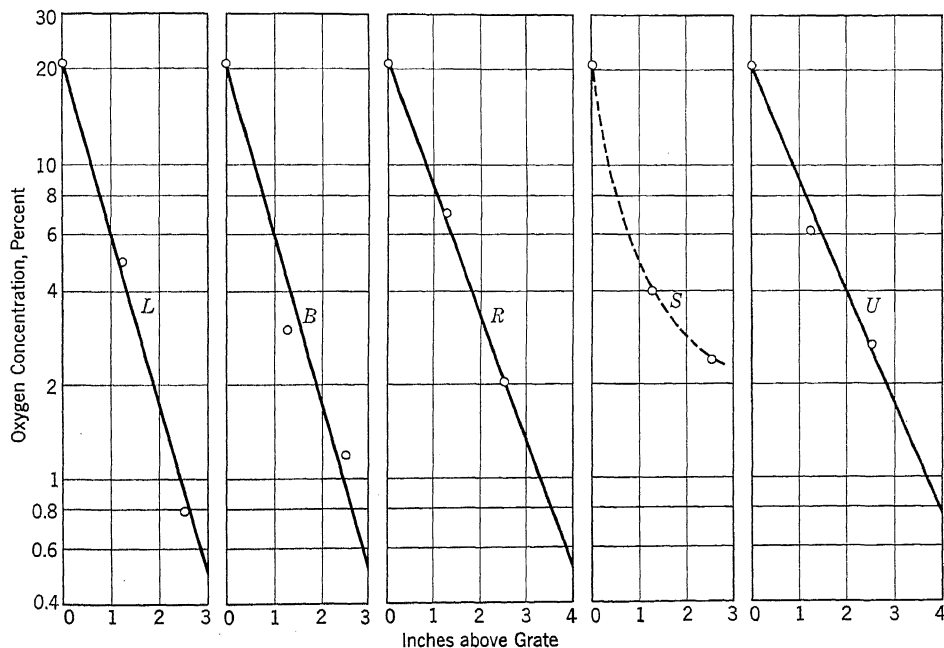


FIG. 7. Gas components in overfeed fuel beds. Coke designations same as in Fig. 3. Air rate (G) = 150 pounds per square foot per hour.

A. Oxygen.

B. (See cut and legend on p. 904.)

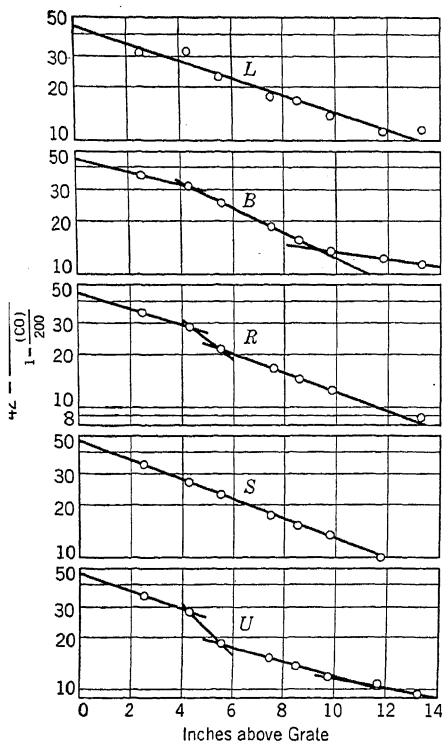


FIG. 7. (See legend on p. 903.)

$$B. \text{ Carbon monoxide as } 42 - \frac{[\text{CO}]}{1 - \frac{[\text{CO}]}{200}}$$

gion in question is close to that in which oxygen is still present in the gas, and it is probable¹⁵⁰ that carbon monoxide formed directly from oxygen, as well as by reduction of carbon dioxide, is not further oxidized in this region. The significance of these effective reaction rates and their relations to other properties of the coke will be treated in more detail in a later section.

Adsorption Tests. The ability of the coke to adsorb water vapor,^{128, 151} carbon

¹⁵⁰ Martin, H., and Meyer, L., *Z. Elektrochem.*, **41**, 136-46 (1935). Grodzowski, M. K., and Chukhanov, Z. F., *Fuel*, **15**, 321-8 (1936). Chukhanov, Z. F., *J. Tech. Phys. (U.S.S.R.)*, **8**, 147-61, 621-32 (1938); *Fuel*, **18**, 292-302 (1939).

dioxide,¹⁵² and methylene blue,¹¹³ especially the first two, may be related to its reactivity, but not much use has been made of these characteristics.

DEGREE OF GRAPHITIZATION

Although the degree of graphitization of a coke is, like its reactivity, a chemical property, rather than a physical one, it has usually been measured by physical methods and has, in fact, frequently been confused with reactivity, to which it is closely related. The early discussions of this subject actually grew out of measurements of the reactivity to gaseous oxidizing agents of different cokes and sought to explain differences among cokes on the basis of differences in the supposed origin of the different portions of the coke.^{98, 153} These controversies have died down as it was recognized that there was no essential difference, except in crystallite size, between "amorphous carbon" and graphite,¹⁵⁴

¹⁵¹ Braunholtz, W. T. K., Nave, G. M., and Briscoe, H. V. A., ref. 79.

¹⁵² Davis, J. D., and Reynolds, D. A., ref. 129. Müller, W. J., and Jandl, E., *Brennstoff-Chem.*, **15**, 305-9 (1935).

¹⁵³ Fischer, F., Breuer, P. K., and Broche, H., ref. 121. Agde, G., and Recke, F., *Brennstoff-Chem.*, **4**, 341-3 (1923). Heyd, F., *ibid.*, **4**, 198-200 (1923). Schreiber, F., *ibid.*, **4**, 273-5 (1923). Anfhäuser, D., *Glückauf*, **60**, 1195-201 (1924). Bunte, K., and Fitz, W., *Gas- u. Wasserfach*, **67**, 241-3 (1924). Thau, A., *Chem. & Met. Eng.*, **30**, 222-7, 306-10, 347-50 (1924). Mezger, R., and Pistor, F., *Gas- u. Wasserfach*, **69**, 1061-6 (1926). Agde, G., and Schmitt, G., *ibid.*, **70**, 1000-3 (1927). Agde, G., and von Lynckner, L., *ibid.*, **70**, 1016-9 (1927). Dent, F. J., and Cobb, J. W., *Colliery Guardian*, **138**, 2208-10 (1929).

¹⁵⁴ Asahara, G., *Sci. Papers Inst. Phys. Chem. Research*, **1**, 23-9 (1922); *Japan J. Chem.*, **1**, 35-41 (1922); *Chem. Abs.*, **17**, 656 (1923). Lowry, H. H., *J. Am. Chem. Soc.*, **46**, 824-46 (1924). Koch-Holm, E., *Wiss. Veröffentlich. Siemens Konzern*, **6**, 188-201 (1927); *Chem. Abs.*, **23**, 317 (1929). Warren, B. E., *J. Chem. Phys.*, **2**, 551-5 (1934). Hofmann, U., and Wilm, D., *Z. physik. Chem.*, **B18**, 401-16

and that all types of black carbon were, at least, precursors of graphite, which might, however, hold in the rings characteristic of aromatic carbon, various amounts of certain elements other than carbon, and, between planes, considerably larger amounts of a wide variety of foreign elements.¹⁵⁵ Thus, it has been recognized that the reactivity of coke, as well as several of its other properties, are strongly influenced, although not completely determined, by its degree of graphitization, which has led to interest in the measurement of this property. Several of the tests that are used appeared prior to the development of the view stated above, so that they are sometimes referred to as reactivity tests. Three types of measurement are common for this purpose: the measurement of electrical conductivity of the granular coke, the measurement by X-ray diffraction of the spacings of atoms in the powdered coke and the apparent crystallite size, and the observation of the rate of attack on the coke of various oxidizing solutions. Other methods that have been used occasionally include selective flotation¹⁵⁶ and observation under polarized light.¹⁵⁷

Electrical Conductivity. It is found that, when an electric current is passed through a compressed column of coke granules, the resistance to current flow, which is greatly affected by the pressure with which the column is compressed at low

pressures, becomes almost independent of the pressure at high pressures. Thus, a lower limit of resistance is approached that is characteristic of the coke and of its particle size. If the particle size is kept constant, the resistance is a characteristic of the nature of the coke. The measurement may be quickly performed and requires relatively little, simple apparatus.^{128, 158}

X-Ray Diffraction. Debye-Scherrer powder photographs of coke by X-rays yield data from which the spacings of atoms in the hexagonal network layers of the graphite-like coke material may be estimated from the average diameters of the halos observed, and the average sizes of the crystallites may be estimated from the width of the halos. These measurements have been used by Šimek and Coufalík and by Riley and his coworkers in attempts to ascertain more about the chemical nature of coke.^{155, 159} The method and calculations are too involved to describe here but may be found in detail in references given in the original papers. Šimek and Coufalík found no relation between the internal surface of the coke calculated from the dimensions of the crystallites of which it is composed and its reactivity; that is, even when the internal surface was calculated, differences in specific reactivity persisted. Riley and collaborators found a continuous growth of the graphitic crystals as cokes or chars were formed from wood, peat, and

(1932); *Kolloid-Z.*, **70**, 21-4 (1935); *Z. Elektrochem.*, **42**, 504-22 (1936).

¹⁵⁵ Hock, H., and Müschenborn, W., *Glückauf*, **70**, 869-74 (1934). Hock, H., and Schrader, O., *Braunkohle*, **35**, 645-50 (1936). Balfour, A. E., Riley, H. L., and Robinson, R. M., *J. Chem. Soc.*, **1936**, 456-61. Blayden, H. E., Riley, H. L., and Taylor, A., *ibid.*, **1939**, 67-75. Riley, H. L., *Chemistry & Industry*, **1939**, 391-8.

¹⁵⁶ Hock, H., and Müschenborn, W., ref. 155.

¹⁵⁷ Ramdohr, P., *Arch. Eisenhüttenw.*, **1**, 669-72 (1928). Koppers, H., and Jenkner, A., *ibid.*, **5**, 543-7 (1932). Hock, H., and Schrader, O., ref. 155.

¹⁵⁸ Koppers, H., and Jenkner, A., ref. 157. Davis, J. D., and Auvil, H. S., *Ind. Eng. Chem.*, **27**, 1196-200 (1935). Balfour, A. E., Riley, H. L., and Robinson, R. M., ref. 155. Bruk, A. S., and Afanas'ev, M. V., *Coke & Chem. (U.S.S.R.)*, **6**, No. 8, 31-6 (1936); *Chimie & industrie*, **38**, 247 (1937). Müller, W. J., and Jandl, E., *Brennstoff-Chem.*, **19**, 29-30 (1938). Blayden, H. E., Noble, W., and Riley, H. L., *J. Iron Steel Inst. (London)*, **139**, 75-98 (1939).

¹⁵⁹ Šimek, B., and Coufalík, F., *Brennstoff-Chem.*, **18**, 213-20 (1937). Blayden, H. E., Riley, H. L., and Taylor, A., *J. Am. Chem. Soc.*, **62**, 180-6 (1940).

bituminous and anthracite coals as the temperature of formation increased. Peat and cellulose showed exceptionally rapid rates of growth when the carbonizing temperature was in the neighborhood of 700° C, a region which has been found to be of special importance in other work, in that the electrical conductivities, reactivities, and susceptibility to attack by liquid reagents of cokes and chars formed below and above this temperature differ markedly.^{51, 128, 160}

Oxidation by Liquid Reagents. Liquid reagents such as sulfuric acid, nitric acid, chromic acid, and acid and alkaline potassium permanganate have long been used to degrade coal and its residues after thermal decomposition to a soluble condition. Occasionally¹⁶¹ the rate of this oxidation has been used in attempts to characterize the reactivity of cokes, when it was found that the rates of production of sulfur dioxide of different cokes, for example, were approximately parallel to the rates of reaction of the same cokes observed with gaseous oxidizing agents at high temperatures, but that they depended almost entirely on the temperature of carbonization and were almost independent of the coal carbonized, as shown in Table 7 (page 40) of reference 51. It was found by Riley and his associates, however, that the rates of formation of carbon dioxide by different cokes subjected to oxidation by chromic acid in a syrupy solution of phosphoric acid at 100° was in the inverse order to that found when the cokes were oxidized by gaseous reagents.¹⁶² This behavior has been interpreted as being due to a reaction between

the elements of graphitic crystallites, which are said to be amphoteric, and the strong acid.¹⁶³ Thus, the method becomes a specific measure of the amount of graphite in the coke as in similar chemical methods for differentiating between graphite and other black carbonaceous materials.¹⁶⁴

It has also been shown by Juettner¹⁶⁰ that successive oxidations of coke by nitric acid and alkaline permanganate lead to the conversion of large percentages of the carbon in carbonaceous materials that have been heated to 700° or above to mellitic acid, the benzenhexacarboxylic acid. Approximately the same percentage yield was obtained as mellitic acid from carbon from any source, provided only that it had been heated to at least 700°; materials that had not been heated so high gave proportionately lower yields, coal producing only a few percent of mellitic acid. Thus, this result also could be used to characterize the graphitic nature of coke, since the appearance of large amounts of mellitic acid indicates that a large proportion of the carbon present had existed in the form of condensed aromatic systems of at least four rings. (See Chapter 9.)

RELATIONS BETWEEN COKE PROPERTIES AND THE SOURCES AND CONDITIONS OF MANUFACTURE OF THE COKE

STRUCTURAL PROPERTIES

Effect of the Coal Composition, Temperature of Carbonization, and Oven Size. The primary influences on the strength and size of coke are the composition of the coal from which it is made and the temperature of carbonization. The dominant effect of the first of these is shown by the fact that the correlation coefficient between the 1½-

¹⁶⁰ Riley, H. L., and Blayden, H. E., *Nature*, **135**, 387-8 (1935). Juettner, B., *J. Am. Chem. Soc.*, **59**, 208-13 (1937).

¹⁶¹ See for example pp. 37-42 of ref. 51.

¹⁶² Riley, H. L., and Blayden, H. E., ref. 160. Blayden, H. E., and Riley, H. L., *J. Soc. Chem. Ind.*, **54**, 159T (1935). Balfour, A. E., Riley, H. L., and Robinson, R. M., ref. 155.

¹⁶³ Riley, H. L., *J. Inst. Fuel*, **10**, 149-56 (1937).

¹⁶⁴ Hofmann, K. A., and Röchling, C., *Ber.*, **56B**, 2071-6 (1923). Ramdohr, P., ref. 157.

inch shatter index of the coke and the carbon content of the parent coal on the dry ash-free basis, for 58 cokes reported by Evans and Ridgion,¹⁶⁵ was 0.796. This is the more remarkable when it is observed that no special pains were taken to insure that these cokes were carbonized at exactly the same temperature, although all were high-temperature cokes, nor to charge the ovens, when they were made, to the same bulk density, although this factor undoubtedly affects the strength of the coke to some extent. Finally, the cokes were made in different kinds of ovens of different sizes, and from coals from all parts of England, including fields in South Wales, Durham, Northumberland, Scotland, and Yorkshire. The correlation permits the expression of the shatter index, y , percent on $1\frac{1}{2}$ -inch, by the equation

$$y = 2.71x - 148.9 \quad (19)$$

where x is the percentage of carbon in the coal on the dry ash-free basis. The standard deviation from this distribution is 5.1 in the shatter index at the center of gravity of the distribution, at 85.8 percent carbon, and increases somewhat either side of this point, as shown in Fig. 8, in which the points representing these data are plotted with the line given by equation 19. The curving lines either side of the central one, which is drawn to fit the equation, are separated from it by distances determined by the standard deviation, so that the band they define should include 68 percent of the points. As a matter of fact, only 11 of the points, or about 19 percent, fall outside these limits. These deviations, which correspond to probable errors of 3.4 to 5.5, are to be compared with the probable error of the shatter test itself, which, as shown

above, is about 1.0 in the $1\frac{1}{2}$ -inch index. It can hardly be doubted, moreover, that, if the comparison had been made on cokes carbonized under controlled conditions, the correlation would be materially improved and the limits of error decreased. This justifies the expectation that, when better data are available, it may become possible to es-

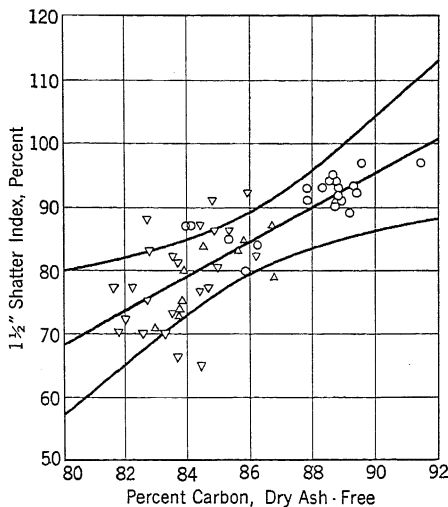


FIG. 8. Relation between percentage remaining on $1\frac{1}{2}$ -inch screen after shatter test and carbon content of the parent coal.¹⁶⁵

timate the strength of coke quite satisfactorily from the analysis of the coal from which it was made and from the conditions of coking.

Equation 19 has been checked for three cokes, whose size analyses after the shatter test are given in Fig. 3 with the designations L , R , and U , made from different samples of the same coal for which the analysis and coking temperature are available. The calculated and observed $1\frac{1}{2}$ -inch shatter indexes are given in Table X, from which it can be seen that the agreement is nearly as good as found for the British coals. When the observed indexes are cor-

¹⁶⁵ Evans, E. C., and Ridgion, J. M., *Iron Steel Inst. (London)*. Special Report 17, 1937, 62 pp., Table 25, p. 39.

TABLE X

CALCULATED AND OBSERVED SHATTER INDEXES
FOR COKES FROM PITTSBURGH COAL

Shatter Index: Percent on 1½-inch

Coke	Calc.	Observed	Corrected for Coking Temperature	
			To 1,040°	To 1,000°
L	80.6	79.6	79.6	80.5
R	81.1	75.0	76	77.8
U	82.6	76.3	78	79.6

rected for temperature of carbonization to 1,040°, which is probably close to the mean for the British cokes, the agreement is greatly improved. The method of making this correction will be discussed below. The dependence of the quality of the coke, as measured by its resistance to shattering or by its size, upon coal analysis has long been recognized and has been the basis of much of the blending procedure in commercial carbonization;^{83, 166} in fact, Gerhard claimed to have used it to improve coke quality as long ago as 1910. The reason for the correlation between the shatter test and the value of the Sheffield swelling index, noted in the discussion of the example of correlations worked out on page 871, now becomes apparent, since it has been shown¹⁶⁷ that the swelling index is also a function of coal analysis.

A correlation similar to that resulting in equation 19 has been worked out in the

¹⁶⁶ Bunte, K., *Gas- u. Wasserfach*, **68**, 82-5 (1925). Gerhard, F., *ibid.*, **68**, 282-3 (1925). Schweder, W., *ibid.*, **70**, 710-2 (1927). Parr, S. W., and Mitchell, D. R., *Ind. Eng. Chem.*, **22**, 1134-5 (1930). King, J. G., *Fuel*, **10**, 521-31 (1931). Pieters, H. A. J., *Rec. trav. chim.*, **50**, 851-5 (1931). Swietoslawski, W., Chorazy, M., and Roga, B., *Przemysl Chem.*, **16**, 141-50 (1932). Mott, R. A., and Wheeler, R. V., ref. 67, pp. 207 ff.

¹⁶⁷ Mott, R. A., and Spooner, C. E., *Fuel*, **16**, 4-14 (1937). Mott, R. A., and Wheeler, R. V., ref. 67, pp. 343-69.

Coal Research Laboratory¹⁶⁸ for the 90 coals carbonized at various temperatures in the BM-AGA Survey of the Coke-Making Properties of American Coals,¹⁶⁹ in which the relation between both the proximate analysis of the coal and the properties of the coke, as well as the variation with temperature, were determined. These data, which include results on a number of blends, appear to support the conclusion, reached above, that the results of blending can be predicted from the analysis of the blend in the same way as for a single coal. The correction of the observed shatter indexes for temperature in Table X was made on the basis of a preliminary examination of these data, which indicated that, if the results of the shatter test were expressed in terms of the characteristics M_s and S_s , which determine the position of the line on probability paper representing the size distribution after shattering, an increase in carbonizing temperature from 1,000 to 1,100° C caused them to decrease by 0.224 and 0.069 inch, respectively. These data showed that increase in carbonizing temperature quite uniformly caused a lowering of the values of both M_s and S_s for all coals at all carbonizing temperatures above 600° C.

In contrast with this result, the strength of the ultimate coke substance increases as the temperature is raised as shown by "micro-strength" indexes^{15, 105} and by true abrasion.¹⁰¹ These facts support the belief that the extent of degradation by shattering is a measure of the extent of fissuring of the coke caused by the loss of volatile matter after the coke has passed through

¹⁶⁸ Lowry, H. H., Landau, H. G., and Naugle, L. L., *Trans. Am. Inst. Mining Met. Engrs.*, **149**, 297-330 (1941).

¹⁶⁹ Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph 5* (1934), 164 pp. Cf. also Fieldner, A. C., et al., *U. S. Bur. Mines, Tech. Paper 601* (1939), 45 pp.

the plastic zone.¹⁷⁰ Warren's results^{105, 171} show variable effects of rate of heating on the strength of the basic coke material, depending on the characteristics of the coals carbonized. The outstanding result, that the strength of coke made from low-rank coal is increased by rapid heating, is supported by the observations on shatter index made by Mott and Wheeler¹⁷² and by commercial practice.¹⁷³

The size and strength of coke are also affected by the size of the ovens in which it is made and by the position in the oven from which it comes.^{99, 174} Although a portion of this dependence may be ascribed to differences in the maximum temperature of carbonization and of the rate of heating associated with those differences of oven dimensions and position, another portion is probably dependent on the bulk density of the coal, which varies from point to point, and on the mechanical pressure to which the coal is subjected during carbonization. Thus, Braunholtz, Nave, and Briscoe found that compressed charges of coal, tamped to high bulk density, produced cokes having lower shatter indexes, but higher true and apparent specific gravities, than top-charged coal,¹⁴ but Mott and Wheeler have stated, "The merits of cake charging are, in fact, few, the original claim made for it, that a better coke would be made from inferior coals, being unfounded except for coals of lowest rank."¹⁷⁵ On the other hand, Evans, discussing the paper by Blayden, Noble, and Riley,¹⁵⁸ remarked that frequently in his experience coke from cake-

charged ovens was preferred for blast-furnace use. Moreover, Riley and collaborators have shown¹⁵ that it is possible, by the application of mechanical pressure of the order of 1 atmosphere, to produce coherent cokes from coals that are normally noncoking or only weakly coking. The initial development of strength by the coke, between the temperatures of 400 and 600° C, was greatly influenced by the magnitude of the external pressure. In this range, increase in pressure always caused an increase in the micro strength of the coke, the most significant effects being produced by pressures up to 50 pounds per square inch; pressures above this up to 500 pounds per square inch had a proportionately smaller effect. Above 650° C, however, the gain in strength was only slightly affected by the external pressure, depending almost entirely on the maximum temperature attained.

Although some operators have found rather important effects of coal size as charged to the ovens on the strength of the coke formed,^{52, 176} these are not usually great unless the coal is very weakly coking, or, as in Davidson's work, very large lump coal is used. Mott and Wheeler¹⁷⁷ have remarked that no advantage in shatter is gained by grinding to finer than 1/4 inch if any one of the coals blended is strongly coking. On the other hand, the size of the coal charged does appear to affect the bulk density of the oven charge, and thus the apparent specific gravity of the coke, the use of double-screened large coal leading to lower bulk density of the charge and lower apparent specific gravity of the coke.^{52, 108}

The Effect of Additions to the Charge. There has been a great deal of interest in

¹⁷⁰ Davidson, W., *Colliery Guardian*, **145**, 1224-8 (1932).

¹⁷¹ Warren, W. B., *Ind. Eng. Chem.*, **30**, 136-41 (1938).

¹⁷² Pages 389-404 in ref. 67.

¹⁷³ Thiessen, G., *Ind. Eng. Chem.*, **29**, 506-13 (1937).

¹⁷⁴ Mott, R. A., and Wheeler, R. V., pp. 18-54, ref. 86.

¹⁷⁵ See p. 388 of ref. 67.

¹⁷⁶ See Schweder, W., in ref. 166. Seyler, H. W., *Coal Mine Mechanization, Yearbook Coal Div., Am. Mining Congr.*, **1933**, 179-83.

¹⁷⁷ See pp. 373-8 of ref. 67.

the addition of coke breeze to the charge supplied to the coke oven, mainly with a view to finding a profitable outlet for the large volumes of breeze that accumulate at plants producing metallurgical coke.^{33, 83, 170, 178} It has usually been found that the addition of breeze, if it is ground fine enough, improves the yield of large coke on carbonization and frequently increases the 2-inch and 1½-inch shatter index. These beneficial effects, however, are accompanied by a decrease in the resistance of the coke to abrasion, whether measured by the tumbler test, the ½-inch shatter-test index, or the departure of the sizing after shatter from a straight line on probability paper. The amount of breeze which may be added to the charge before this effect becomes serious depends on the coking properties of the coal; in the example reported by Biddulph-Smith, when a very strongly coking Durham coal was used, even 25 percent of breeze could be added to the coal with an apparent improvement in the percentage on 1½-inch after the tumbler test from 90.0 percent without addition to 94.2 percent with breeze. On the other hand, Seyler found that the optimum addition, with a high-volatile Pittsburgh coal, was about 6 percent.

The effect of varying amounts of breeze added is typified by the results obtained by Pfluke, Sedlachek, and Huyck in very careful full-scale trials.¹⁷⁹ In this work various amounts of coke breeze, ground and sieved to various degrees of fineness, were added to two coals at different plants and car-

bonized in regular practice in gas-plant by-product ovens. In one plant, a mixture of 80 percent Powellton and 20 percent Pocahontas pulverized coal was normally carbonized in 18-ton ovens; in the other, crushed straight Pittsburgh coal was coked in 6.8-ton ovens. The analyses of the coals are given in Table XI. From 1 to 5 per-

TABLE XI

PROXIMATE ANALYSES OF COALS CARBONIZED WITH COKE BREEZE ADDITIONS¹⁷⁹

Coal	Powell-ton	Poca-hontas	Pitts-burgh
Proportion in mixture, percent	80	20	100
Moisture, percent	3.5	4.7	3.5
Volatile matter,* percent	33.6	17.6	34.1
Fixed carbon,* percent	61.2	76.6	59.2
Ash,* percent	5.2	5.8	6.7

* Dry basis.

cent of coke breeze, ground to pass ½²-, ¼⁶-, ⅛⁸-, ⅜¹⁶-, and ¼⁴-inch, was carefully mixed with the 40,000-pound charges; the coke produced was carefully sampled, sieve analyses were made including screens down to No. 6 mesh (3,360 microns), and shatter tests were made. In the second report (1937), the effect of crushing the coke produced was also investigated and the process was considered from the point of view of net decrease in breeze to be disposed of. This portion of the subject is outside the scope of the present report, but it is to be noted that this question and the problem of the economics of the process, treated by these authors and by Killing and Elbert,¹⁷⁸ determine the commercial feasibility of this method of breeze disposal.

The data from the shatter tests, plotted to probability coordinates, yield the characteristics of the distribution M_s and S_s ,

¹⁷⁸ Mott, R. A., and Wheeler, R. V., pp. 184-94 of ref. 86; pp. 426-58 of ref. 67. King, J. G., ref. 166. Biddulph-Smith, T., *Iron & Coal Trades Rev.*, **122**, 44-5 (1931); *Blast Furnace Steel Plant*, **21**, 471-3, 479, 481 (1933). Seyler, H. W., ref. 176. Killing, A., and Elbert, W., *Glückauf*, **70**, 162-4 (1934).

¹⁷⁹ Pfluke, F. J., Sedlachek, A. C., and Huyck, A. B., *Proc. Am. Gas Assoc.*, **1936**, 771-92, **1937**, 619-48.

which are plotted against the amount of breeze added in Figs. 9 and 10, in which each curve shows the effect of one size of breeze. The irregularities in the curves

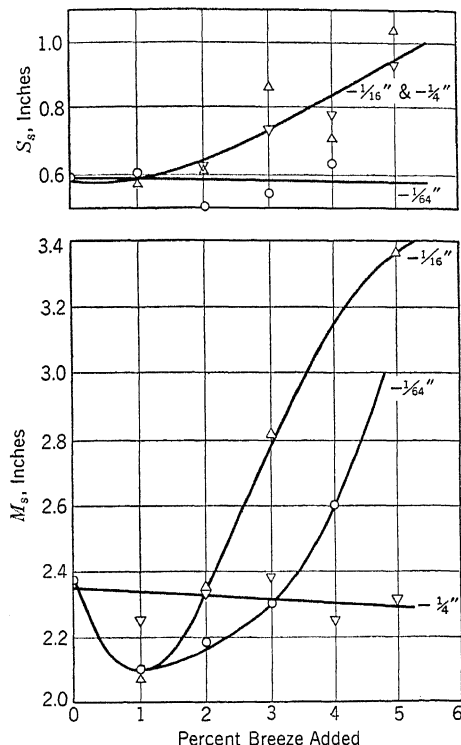


FIG. 9. Effect of additions of coke breeze to coal mixture on the shatter test of coke. Powellton-Pocahontas coal mixture.¹⁷⁰

- \circ Breeze size $\frac{1}{16}$ inch.
- \triangle Breeze size $\frac{1}{8}$ inch.
- ∇ Breeze size $\frac{1}{4}$ inch.

suggest that the conditions of carbonization may not have been entirely under control. Breeze addition caused first a slight decrease and then a marked increase in the mean size of the shattered coke from the Powellton-Pocahontas mixture, a relatively strongly coking coal, for all breeze sizes smaller than $\frac{1}{4}$ -inch, which had not reached the maximum within the range of

the amounts added, up to 5 percent; on the other hand, only the smallest size, through $\frac{1}{32}$ -inch, caused an increase in the mean size of shattered coke from Pittsburgh coal, and the maximum effect was reached at about 3 percent of breeze added. The values of S_8 increase continually, and

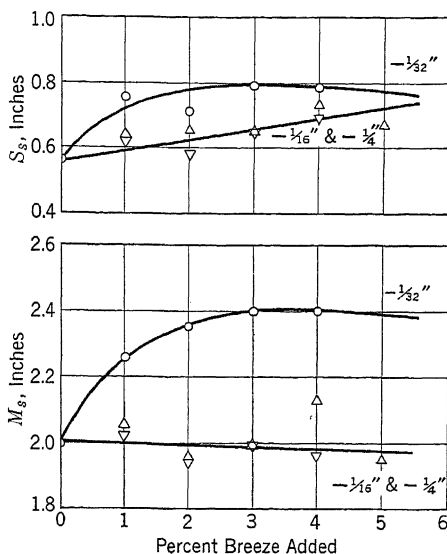


FIG. 10. Effect of additions of coke breeze to coal mixture on the shatter test of coke. Straight Pittsburgh coal.¹⁷⁰

- \circ Breeze size $\frac{1}{32}$ inch.
- \triangle Breeze size $\frac{1}{16}$ inch.
- ∇ Breeze size $\frac{1}{4}$ inch.

almost linearly, with approximately the same slope for both coals and all breeze sizes. This effect may be significant in view of one of the preliminary conclusions drawn from the work on the correlation of coke properties with coal analysis, etc., mentioned above as being in progress in the Coal Research Laboratory. It appears that the mean size of shattered coke tends to increase not only with the fixed carbon of the coal, but also with its ash; but the spread, S_8 , tends to be independent of the fixed carbon, and to depend only on the ash

content with which it increases and on the temperature of carbonization. This suggests that, in its effect on the shatter test of the coke, breeze addition acts in the same way as addition of ash would.

The effect of large additions of noncoking materials to coal on the shatter test of the coke can be seen from the results of tests made by Davidson,¹⁸⁰ some of whose data

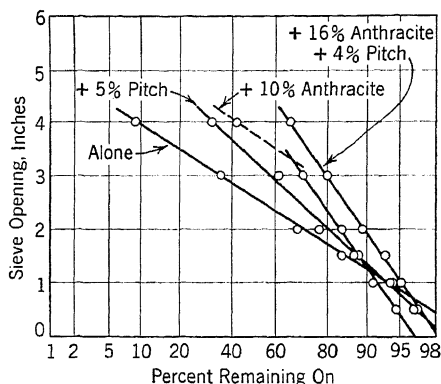


FIG. 11. Effect of large additions of non-coking materials on size distribution of coke after shattering.¹⁸⁰

on shattered coke are shown in Fig. 11. It is evident that pitch behaves, just as does anthracite, as a noncoking addition; and that, though both addition agents increase the proportion of large-size coke produced, they do so only at the cost of a large increase in the value of S_g , which indicates that the range of sizes in a bed of this coke would be extremely large and that any additional handling or abrasion would increase it very rapidly. Hence, a bed formed of this coke would tend to have a low void volume and, in spite of its large average size, would have a high resistance to air flow.

Mott and Wheeler discussed, in addition to their extensive work on blending with

fusain and high- and low-temperature coke breeze,¹⁷⁸ the effect of the addition of small amounts of organic solvents¹⁸¹ on the shatter tests of coals carbonized at low temperatures, but the results do not appear to be conclusive. It may be noted here that those authors have reported a great deal of work, to only a portion of which reference has been made, whose significance is not at present apparent. Many of their results, however, may become significant at a later date when the field is more completely explored.

REACTIVITY

Effect of Conditions of Carbonization and Correlation with Other Properties of the Coke. The most important factor affecting the reactivity of coke is the maximum temperature to which it was heated during carbonization,^{51, 98, 101, 113, 125, 128, 132} the reactivity of cokes from all coals decreasing markedly as the temperature of carbonization increases. This effect is illustrated by Table XII, taken from the paper by Davis and Fieldner.¹²⁸ Drakeley and Wilkins¹¹³ found an approximately linear relation between the ignition points of cokes and the maximum temperatures at which they were carbonized, while Bähr and Fallböhrer¹⁰¹ remarked that, in the absence of catalysis by ash constituents, the ignition point and reactivity are determined by the temperature of carbonization.

Since this is so, obviously the reactivity of coke will be closely correlated with all other coke properties that are temperature dependent. Chief among these is the hydrogen content of the coke, which, for high-temperature cokes, at least, depends only

¹⁸¹ See pp. 326-42 of ref. 67.

¹⁸² Müller, W. J., and Jandl, E., refs. 127 and 152. *Brennstoff-Chem.*, **14**, 341-3, 343-7, 421-4, 441-4 (1933). Hoek, H., and Schrader, O., ref. 155. Neumann, B., and van Ahlen, A., *Brennstoff-Chem.*, **15**, 5-10 (1934). Nettlenbusch, L., ref. 121.

¹⁸⁰ Davidson, W., *J. West Scot. Iron Steel Inst.*, **43**, 118-24 (1936).

TABLE XII

 DEPENDENCE OF VARIOUS CRITERIA OF REACTIVITY, ETC., ON THE COAL AND THE CARBONIZING TEMPERATURE ¹²⁸

Column No.	Heading									
1	Carbonizing temperature, °C									
2	Volatile matter, percent, dry basis									
3	Ash content, percent, dry basis									
4	Carbon, percent, dry basis									
5	Hydrogen, percent, dry basis									
6	Ash-fusion temperature, average for all cokes from same coal, °F									
7	Reactivity to carbon dioxide, percent									
8	Ignition temperature, °C									
9	Minimum air rate (MAR) required to support combustion, cubic feet per hour									
10	Electrical resistivity, ohms per meter per square millimeter cross section									
11	Hygroscopicity, percent									
1	2	3	4	5	6	7	8	9	10	11
<i>Illinois No. 6 (Coal No. 10)</i>										
500	8.9	16.6	73.8	2.9		62.8	374	1.18		5.3
600	5.0	17.6	75.3	2.1		65.8	390	1.40	154 × 10 ⁶	5.7
700	2.1	18.7	76.1	1.4	2,400	66.9	441	1.84	93,800	6.3
800	1.2	18.8	77.0	0.9		58.7	459	2.20	2,060	6.4
900	1.3	18.9	78.0	0.5		39.9	470	3.48	361	3.4
1,000	1.0	18.5	79.0	0.5		22.9	480	4.08	191	1.3
1,100	0.9	18.7	79.5	0.3		20.1	501	4.93	162	0.7
<i>Green River (Coal No. 21)</i>										
500	10.9	9.2	80.2	3.1		61.9	353	1.09		4.8
600	6.1	9.9	82.1	2.3		59.4	410	1.50	19.5 × 10 ⁶	5.3
700	2.7	10.8	83.1	1.3		54.7	429	2.03	5,390	5.4
800	1.5	10.8	84.1	0.9	2,320	38.4	454	2.48	831	3.5
900	0.6	11.2	84.2	0.7		12.7	498	3.38	245	0.8
900 (18")	0.8	10.8	84.9	0.6						
1,000	0.4	11.1	85.1	0.4		6.4	558	4.15	158	0.2
1,000 (18")	0.7	10.8	85.6	0.4						
1,100	0.3	11.4	85.8	0.3		4.9	600	4.77	122	0.1
<i>Pittsburgh Coal (Coal No. 28)</i>										
500	9.8	6.7	84.2	3.2		54.1	420	1.65		3.6
600	5.6	7.1	85.8	2.4		51.8	455	2.05	14.8 × 10 ⁶	4.6
700	2.7	7.4	87.6	1.5		50.7	478	2.60	7,660	3.8
800	2.0	7.4	88.2	1.2	2,770	39.3	550	3.65	471	1.8
900	0.6	7.8	88.8	0.7		27.9	570	4.13	192	0.4
900 (18")	0.8	7.6	89.0	0.6						
1,000	0.4	7.8	89.3	0.4		17.7	608	4.40	128	0.3
1,000 (18")	0.3	7.7	89.4	0.4						
1,100	0.4	7.7	89.8	0.3		11.5	624	4.95	86	0.1
<i>Sewell (Summerlea) (Coal No. 27)</i>										
500	7.3	2.8	89.0	3.1		34.6	425	1.60		3.2
600	4.1	2.9	90.7	2.2		33.3	458	2.20	71,200	4.7
700	2.6	3.0	92.1	1.5		33.9	493	2.55	2,700	3.5
800	1.9	3.5	92.4	1.2	2,730	27.9	508	2.90	316	1.5
900	0.7	3.2	93.8	0.7		12.1	545	3.10	132	0.6
900 (18")	0.6	3.1	93.9	0.8						
1,000	0.5	3.0	94.4	0.5		6.6	555	3.35	94	0.2
1,000 (18")	0.3	3.1	94.3	0.4						
1,100	0.3	3.0	94.7	0.3		4.4	573	3.80	68	0.1
<i>Sewell (Cranberry) (Coal No. 26)</i>										
500	8.3	2.3	88.8	3.5		44.1	405	1.45		
600	4.7	2.5	90.6	2.4		44.0	420	1.90	1,095,000	
700	2.3	2.6	92.3	1.5		37.5	452	2.48	3,590	
800	2.2	2.7	92.6	1.2	2,520	31.7	479	2.65	461	
900	1.1	2.5	93.8	0.9		13.2	511	2.90	148	
900 (18")	0.6	2.5	94.1	0.8						
1,000	0.8	2.7	94.2	0.5		4.3	543	3.15	92	
1,000 (18")	0.5	2.6	94.5	0.5						
1,100	0.6	2.5	94.8	0.4		5.0	593	3.15	75	

on the temperature of carbonization and is independent of the hydrogen content of the original coal.^{168, 183} This effect is so regular that Lowry and coworkers¹⁶⁸ have given the equation:

$$\log H = 1.42 - 0.00173T \quad (20)$$

where H is the hydrogen content of the coke on the dry, ash-free basis in percent and T is the carbonization temperature, which represented their data within a probable error of 0.09 percent from 600 to 1,100° C, and have suggested that the hydrogen content of the coke may conveniently be used as a thermometer to measure the maximum temperature of carbonization. It is, therefore, not surprising that a relation has been observed between the reactivity of coke and its hydrogen content.^{51, 118} The reactivity is also related to the true density of the coke,^{101, 184} which, if corrected for ash, also appears to depend only on the maximum temperature of carbonization.¹⁶⁸ Moreover, Davis and Reynolds¹²⁹ found that reactivity decreased as the bulk density of the coke increased, although Perrott and Kinney¹⁸ found that the combustibility, defined as the distance from the tuyères at which carbon dioxide disappears in the blast furnace, was independent of the porosity of the coke.

In view of their similar dependence on temperature (and probably also on the parent coal, although this is less certain), it appears that the reactivity and density of a coke are very strongly dependent on its degree of graphitization, and for many purposes it is immaterial which one of the measurements of these three classes is used as a criterion of coke quality. As noted by

Mott and Wheeler,¹⁸⁵ the true density is but one of the indexes of the degree of graphitization of a coke, so it is to be expected that the other indexes of this characteristic should also be temperature dependent and exhibit a close correlation with the reactivity of the coke.^{51, 121, 155, 158, 162, 163} In fact, the electrical conductivity has been used¹⁸⁶ as a measurement from which the combustibility could be calculated because it is so much more rapid and easy than the combustibility determination. This cannot be a valid procedure generally, although it may be permissible for a single group of coals, because the ash may affect the two determinations in unrelated ways. The reactivity may be influenced by catalytic activity of the ash independently of the degree of graphitization, so that, when this specific property is desired, it must be measured directly. In this connection it should be mentioned that not all the tests of reactivity are equally appropriate for the assessment of the effect of ash constituents. When the active agent is iron, initially present in the form of ferric oxide, low-temperature combustibility and ignition-point tests will not detect its effect, since the iron becomes active, as shown below, only when present as the metal or as ferrous oxide, and these forms appear only by reduction at temperatures above those used for these tests and in a reducing atmosphere. Hence, if catalysis by iron is believed to be present in the process, the reactivity test with carbon dioxide is the only appropriate one.

When a number of rather similar coals are compared by different reactivity tests, it is unlikely that they will be placed in exactly the same order by all of them. This is probably due to the facts that in most

¹⁸³ Mott, R. A., and Wheeler, R. V., pp. 312-6, ref. 67. Gabinskii, Y. O., and Krym, E. S., *Khim. Tverdogo Topliva*, **7**, 650-63 (1936).

¹⁸⁴ Hock, H., and Schrader, O., ref. 155.

¹⁸⁵ Mott, R. A., and Wheeler, R. V., pp. 318-25 of ref. 67.

¹⁸⁶ Schairer, W., *Gas- u. Wasserfach*, **80**, 422-4 (1937).

such tests not all the physical factors which determine the effective reaction rates are eliminated or even evaluated, or that the tests measure some combination of properties rather than any one specific reaction rate. A good example of this state of affairs is given by a report to the American Gas Association in 1926,^{149, 187} in which the results of tests by several different groups of experimenters were reported on five cokes made in different plants from the same coal at nearly the same temperatures. In Table XIII is given the order in which

of the various cokes was much the same, there is practically no agreement among the orders of the different groups. It is significant, however, that the coefficients μ_1/G and μ_2/G , calculated as described above (page 903), are simply related to physical properties of the coke but not to any of the chemical reactivity measurements. As shown in Figs. 12 and 13, μ_1/G is nearly a linear function of the apparent specific gravity of the coke, decreasing as it increases, whereas μ_2/G is a linear function of the volume of voids in a bed of the coke

TABLE XIII

ORDER OF MERIT OF FIVE COKES BY DIFFERENT TESTS^{129, 187}

Investigators and test	Order of Increasing Reactivity				
	1	2	3	4	5
Davis and Greene—reactivity to air	<i>B</i>	<i>S</i>	<i>L</i>	<i>U</i>	<i>R</i>
reactivity to carbon dioxide	<i>B</i>	<i>S</i>	<i>L</i>	<i>U</i>	<i>R</i>
reactivity to water vapor	<i>B</i>	<i>L</i>	<i>S</i>	<i>U</i>	<i>R</i>
Haslam, Ward, and Boyd					
Steam decomposition at 4 pounds per square foot per minute	<i>B</i>	<i>L</i>	<i>U</i>	<i>R</i>	<i>S</i>
Ratio $\frac{\text{CO}}{\text{CO} + \text{CO}_2}$	<i>L</i>	<i>S</i>	<i>U</i>	<i>B</i>	<i>R</i>
Haslam and Ward					
Air rate to maintain fire	<i>R</i>	<i>U</i>	<i>B</i>	<i>L</i>	<i>S</i>
Time required for ignition	<i>R</i>	<i>U</i>	<i>S</i>	<i>B</i>	<i>L</i>
Nicholls, Orr, and Brewer					
Time to burn first 6 pounds	<i>U</i>	<i>R</i>	<i>L</i>	<i>S</i>	<i>B</i>
Unburned combustible in residue	<i>R</i>	<i>U</i>	<i>S</i>	<i>L</i>	<i>B</i>

the different cokes, designated by the letters *B*, *L*, *R*, *S*, and *U*, were placed by the different tests. It will be observed that, although, where several tests were performed by a single investigator, the order

of the size used in the burning test, decreasing as the void volume increases. These quantities are probably the most significant ones for the use of the coke as fuel in heating furnaces, for gas producers, or for the blast furnace, so that their dependence on physical properties of the coke is strong support for the position taken on pages S71-6 of this report, that the structural properties of the coke were the most important criteria of satisfactory operation in

¹⁸⁷ McBride, R. S., *Proc. Am. Gas. Assoc.*, **1926**, 980-7. Beebe, A. M., *ibid.*, **1926**, 988-1082. Haslam, R. T., Ward, J. T., and Boyd, J. H., *ibid.*, **1926**, 1083-104. Haslam, R. T., and Boyd, J. H., *ibid.*, **1926**, 1120-7. Nicholls, P., Orr, M. L., and Brewer, W. M., *ibid.*, **1926**, 1144-59. Davis, J. D., and Greene, J. W., ref. 129.

its use. The simplicity of the relations illustrated in Figs. 12 and 13 suggests that the determination of the coefficients μ_1/G and μ_2/G may be somewhat less subject to adventitious effects than the reactivity determinations.

The data given in Table XII show that the reactivity of coke, and the related quan-

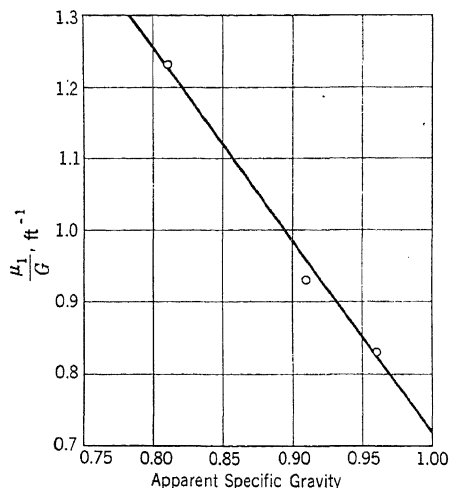


FIG. 12. Relation between reaction rate coefficient (oxygen) and apparent specific gravity of coke. $G = 150$ pounds per square foot per hour.

ties, electrical conductivity and adsorptive power, are not uniquely determined by the temperature of carbonization, but that the nature of the parent coal exerts a considerable effect. Of cokes made at the same temperature, those produced from the lowest-rank coal have the highest reactivity. This is parallel to the variation with rank of the reactivity of the coal itself, which apparently persists throughout the heat treatment of the fuel. By a process involving a preliminary partial oxidation¹⁸⁸ which appears, effectively, to reduce the

¹⁸⁸ Lesher, C. E., *Trans. Am. Inst. Mining Met. Engrs.*, **139**, 328-63 (1940).

rank of the coal, it is possible to produce a semicoke from Pittsburgh coal having a reactivity equal to that produced by the same process, without the oxidation step, from Illinois coal. Thus, Disco from Pittsburgh coal had a value for T_{15} of 205°, and that from Illinois coal had T_{15} equal to 210° C.

The dependence of the reactivity of the coke on the parent coal has been noticed by several authors,^{19, 134, 98, 189} some of whom, however, have not entirely excluded the effect of temperature of carbonization. In this class are the data of King and Jones,

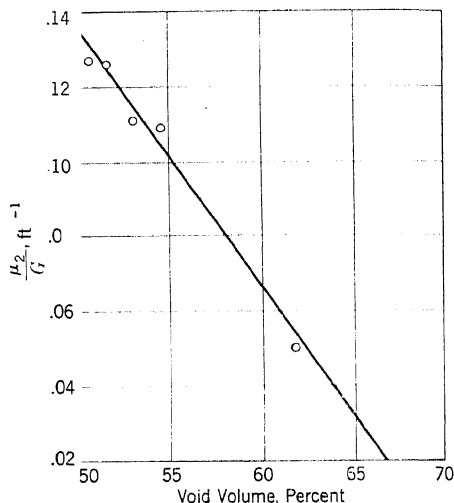


FIG. 13. Relation between reaction rate coefficient (carbon dioxide) and void volume of the bed. $G = 150$ pounds per square foot per hour.

who gave values of 2-inch shatter index, which may be taken as representing the properties of the parent coal, and of reactivity by the Fuel Research Board method for 41 cokes. An attempt to treat these data by statistical methods has shown that, for cokes from all but Durham coals, there is no significant relation between shatter in-

¹⁸⁹ Hock, H., and Schrader, O., ref. 155.

dex and R_{III} , the reactivity index, but for the Durham cokes, the reactivity increases in proportion to the shatter index at the rate of 0.48 point in R_{III} per point increase in shatter, with a correlation coefficient of 0.961. This very high coefficient indicates that the relationship is almost certainly real for this group of cokes and suggests not that it is due to a similar dependence of the shatter index and the reactivity on the coal composition, but that this group of coals may be considered as a single one, and the relationship between the two indexes may be due to their mutual dependence on the temperature of carbonization. This indication is supported by the facts that the correlation coefficients for the other cokes, from South Wales and Yorkshire where the variety of coals used for coking is greater, are not significant, and that the correlation coefficient for all 41 cokes, which is -0.416 , though significant in magnitude, has the opposite sign from that for the Durham coals, so that the apparent significance appears to be due to the heterogeneity of the populations from which the data were drawn. That there is a small, but significant, correlation between shatter index and reactivity is supported by work on a number of blast-furnace cokes in the Coal Research Laboratory and should be expected since, as shown above, both factors decrease with an increase of carbonizing temperature for all coals.

Effect of Inorganic Additions to the Coke. The history of additions of inorganic materials to fuels for the purpose of improving their combustion properties is almost as old as the history of the fuel-burning art, patents being reported by Taylor and Neville¹⁹⁰ from as far back as 1867. Although some of the additions have an undoubted effect on the reactivity of

high-temperature cokes, as measured by their rates of reaction with oxidizing gases, it has not been demonstrated that the effect on reactivity is reflected in burning characteristics in ovens or furnaces.¹⁹¹ This, of course, is to be expected, since with deep fuel beds almost all the oxygen leaving the bed is in the form of carbon monoxide, and even an infinite reactivity could not greatly increase the rate of burning, and even with comparatively shallow beds the increase of burning rate with reactivity is proportional to the increase of a quantity like $(1 - e^{-x})$ with x , when x is relatively large. Thus, the only occasions when increases of reactivity by the use of addition agents, or by any other means, for that matter, would be expected to be of value are those in which reactions at low temperature are significant, as in the ignition of the fuel, and those in which the gasification zone is limited, as in automotive gas producers, or the rate of blast is required to be extremely great as in high-duty water-gas generators. This expectation is confirmed by Nicholls' finding¹⁹¹ that the rate of ignition in underfeed burning is increased by the addition of 0.2 percent soda, although larger applications caused a decrease in ignition rate because of the method of application, which produced an external coating on the coke, and the fact that the only use for which coke containing addition agents is produced commercially¹⁹² is for domestic fuel in open grates, where, as mentioned above (page 874), the problem of ignition of the fuel is a very pressing one.

The most effective catalysts for coke are the metals of the alkali group, usually applied as the carbonates,^{38, 130, 134, 193} al-

¹⁹⁰ Taylor, H. S., and Neville, H. A., *J. Am. Chem. Soc.*, **43**, 2055-71 (1921).

¹⁹¹ Nicholls, P., *U. S. Bur. Mines, Bull.* **404** (1937), 158 pp.

¹⁹² Brewin, W., and Mott, R. A., ref. 50.

¹⁹³ Cobb, J. W., and Sutcliffe, J. A., Branson, W. R., and Dent, F. J., *Trans. Inst. Gas Engrs.*, **1926-7**, 333-402; *Fuel*, **6**, 449-73 (1927); *Gas*

though other salts such as the sulfate, chloride, and cyanide have been used, as well as the oxide. Kröger has shown that the effectiveness of the alkalis increases in the order lithium, sodium, potassium, i.e., in the order of their atomic weights. Sutcliffe and Cobb showed that the acid ion associated with the metal had only a slight effect on the efficacy of the addition agent; Branson and Cobb, King and Jones, and Neumann and van Ahlen showed that calcium, as calcium oxide, was less effective than soda. Askey and Doble, however, showed that a portion of the soda could be replaced by lime, when it became necessary to add only about $\frac{1}{2}$ percent by weight of soda to secure the maximum activation of the reaction.

In spite of the large amount of work that has been done with these addition agents, it is difficult to estimate, quantitatively, the effect of a given amount of addition because the reactivity tests made on the activated cokes have generally yielded little information concerning the actual change in the chemical reaction rates secured. The effect of the addition is not proportional to the amount added but is large at first and then

falls off with larger additions. Heinze and Farnov¹²⁴ have found that, for additions greater than 10 percent, the reactivity may even be decreased. This probably is due to the effect observed by Nicholls¹²¹ of shielding of the coke surface by the addition agent. Adadurov and his collaborators¹²³ and Sebastian¹²⁴ have observed that, if the reaction rates of coke are plotted against the inverse absolute temperature according to the Arrhenius representation, treatment of the fuel with alkali raises the curve but leaves its slope unchanged; hence, the temperature coefficient and heat of activation remain unchanged by the activation. From Fig. 4 of Sebastian's paper it can be estimated that the treatment of a high-temperature coke with 3 percent of soda increased the reaction rate by a constant ratio over the temperature range studied, and that this ratio was equal to 20.3 at an oxygen partial pressure the same as that of air, i.e., 0.207. The last qualification is essential because it was shown in the same work that after activation the reaction of oxygen with coke was no longer of the first order but decreased from first order at low oxygen concentrations toward zero order at oxygen pressures higher than atmospheric. It was noted that this behavior is characteristic of reactions that take place through an adsorbed layer.

White and his coworkers¹²⁵ have set up a mechanism for the activating effect of soda, with which Kröger and his associates are in agreement. They believed that the soda is reduced to metallic sodium in the region where activation occurs by reduction by the carbon present, and that the sodium then vaporizes and is transported to cooler parts of the bed where it can react with carbon dioxide in the gases and again be

J., 182, 946-51 (1938). Dent, F. J., ref. 121. Fox, D. A., and White, A. H., *Ind. Eng. Chem.*, **23**, 259-66 (1931). Moore, B., and Wevell, G. J., *J. Soc. Chem. Ind.*, **50**, 229-42T (1931). Fischer, F., Pichler, H., and Reder, R., *Brennstoff-Chem.*, **13**, 346-50 (1932). Kröger, C., and Fingas, E., *Z. anorg. Chem.*, **212**, 269-83 (1933). Neumann, B., and van Ahlen, A., ref. 182. Weiss, C. B., and White, A. H., *Ind. Eng. Chem.*, **26**, 83-7 (1934). Askey, P. J., and Doble, S. M., *Fuel*, **14**, 197-201 (1935). Brewer, R. E., and Reyerson, L. H., ref. 122. Adadurov, I. E., Grigor'ev, B. A., and Sergeeva, N. G., *J. Applied Chem. (U.S.S.R.)*, **7**, 303-11 (1936); *Chem. Abs.*, **31**, 2786 (1937). Heinze, R., and Farnov, H., ref. 124. Foxwell, G. E., *J. Inst. Fuel*, **10**, 287-8 (1937). Stubbs, A. E., *ibid.*, **10**, 125-48 (1937). Kröger, C., and Melhorn, G., ref. 122. Newall, H. E., ref. 123. Kröger, C., *Angew. Chem.*, **52**, 129-39 (1939). Golovaty, R. N., *J. Applied Chem. (U.S.S.R.)*, **12**, 1178-86 (1940); *Chem. Abs.*, **34**, 3053 (1940).

¹²⁴ Sebastian, J. J. S., *Preprints Symposium on Combustion of Solid Fuel*, Am. Chem. Soc., Boston, September, 1939, pp. 37-40.

deposited as soda. This mechanism was supported by evidence that soda had migrated as vapor at the temperatures of the experiments, which could have happened only if metallic sodium were present. Just how the metallic sodium increases the speed of the reaction is not certain, but it is suggested that it may, in effect, clean the carbon surfaces of an adsorbed oxide layer, thus increasing the surface available for reaction.

Iron is also a very effective catalyst, especially in the high-temperature gasification reactions.^{101, 124, 195} It was found by King and associates, however, that only easily reducible iron, i.e., ferric oxide or ferrous sulfide, was effective in catalyzing the reaction $C + CO_2 = 2CO$, and then only when the iron was exposed to a reducing atmosphere at high temperature long enough to produce the lower oxide or metallic iron. In the Fuel Research Board reactivity test, the sample is heated in a nitrogen atmosphere for an hour before the test is performed, allowing time enough for this reduction to take place. The first reading made, giving a high reading on cokes containing iron, is called R_I , but it is found that this high value is not maintained. With continued passage of carbon dioxide the iron is reoxidized to the ferric state, when a much lower value of reactivity, called R_{III} , is observed. In confirmation of this mechanism, Bähr and Fallböhmer¹⁰¹

found that iron did not affect the ignition-point observation, when it was added as ferric oxide, although it did affect the reactivity to carbon dioxide. The explanation for these facts is that the temperature was never high enough in the ignition-point test, nor was a reducing atmosphere present, to reduce the iron to the ferrous state. Bähr and Fallböhmer also observed that silica added to coke had a negligible effect on the reactivity, as was also found by Neumann and van Ahlen, what effect there was being negative; when both silica and iron were added, however, the iron was no longer effective in increasing reactivity unless the determination was made at temperatures above 1,100° C. Thus, it appears that silica is able to react with iron, probably to form an iron silicate, which removes the iron as an effective catalytic agent.

Several other materials have also been examined for catalytic effects. Among these are manganese dioxide, found by Bähr and Fallböhmer to have a slight effect, and by King and Jones¹³⁴ to have none, and cupric oxide and zinc oxide, found by Bähr and Fallböhmer to have a small and no effect, respectively. Neumann and van Ahlen and Golovaty found that both silica and alumina lowered the reactivity of coke; Fischer, Pichler, and Reder found alumina to be more effective than iron. After investigating the effects of the oxides of aluminum, cobalt, manganese, titanium, uranium, iron, nickel, chromium, and copper, whose effectiveness they found to increase in the order given, Kröger and Melhorn¹²² developed a binary catalyst of potassium oxide with cuprous oxide that produced the greatest catalytic effect of any compound they investigated.

CONCLUSIONS

From this discussion it is evident that, although many methods of measurement of

¹⁹⁵ Bähr, H., ref. 121. Cobb, J. W., and Sutcliffe, J. A., Branson, W. R., and Dent, F. J., ref. 193. Nettlenbusch, L., ref. 121. King, J. G., Jones, J. H., and Sinnatt, F. S., *Dept. Sci. Ind. Research (British), Fuel Research Tech. Paper 25* (1930), 42 pp. Luyken, W., and Bierbrauer, E., *Arch. Eisenhüttenw.*, **4**, 505 (1931); *Stahl u. Eisen*, **51**, 739 (1931). Moore, B., and Wevell, G. J., ref. 193. Fischer, F., Pichler, H., and Reder, R., ref. 193. Neumann, B., and van Ahlen, A., ref. 182. Adadurov, I. E., Grigor'ev, B. A., and Sergeeva, N. G., ref. 193. Šimek, B., and Coufalík, F., ref. 159. Kröger, C., and Melhorn, G., ref. 122. Golovaty, R. N., ref. 193.

coke properties are available, and there is even some information on how those properties may be influenced, there is little real knowledge of whether it would be beneficial or not to produce cokes having specific characteristics. Apparently, the greatest need at present is for an extension of the work of correlating the measured properties of coke with its behavior in the various processes in which it is used. A device for correlating this information has been demonstrated in this report.

Although, as mentioned above, some information on how the properties of coke may be influenced is available, probably a good deal more has been recorded in the literature that has not yet been correlated with what is recognized as pertinent. Hence, it seems desirable that more effort be expended on the correlation of the data already published so that all the material

available is brought to bear on each question at issue. Only in this way can the appropriations available for research, always too much limited, be spent to best advantage.

The information on methods of influencing coke properties by changes in methods of coke production is, to a great extent, expressed in terms of the effects of changes in the fundamental variables of the production process, not in terms of the controllable variables of practice. Since the fundamental variables, like maximum temperature of carbonization and rate of heating, cannot always be controlled, the effect of changes in coking practice cannot always be predicted. Therefore, very likely the most profitable present lines of investigation on coke concern the mechanism of its production rather than, directly, methods of influencing its properties.

BOOK INDEX

This index lists alphabetically by authors the titles of books cited in the text.

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